THE DEVELOPMENT OF MATERIALS FOR CARBON DOUBLE-LAYER SUPERCAPACITORS

DERRICK DesROCHES

The Development of Materials for Carbon Double-Layer Supercapacitors

Derrick DesRoches

A thesis submitted to the
School of Graduate Studies
in partial fulfilment of the
requirements for the degree of
Master of Science

Department of Chemistry, Faculty of Science
Memorial University of Newfoundland
St. John's, Newfoundland
January, 2010

ABSTRACT

The electrochemical properties of porous carbon electrodes were tested by both cyclic voltammetry and impedance spectroscopy. By varying the type/amount of binder (Nafion, Teflon, sol-gel) different capacitance values and mass loadings were observed. As these electrodes were being developed for supercapacitor applications, the mass loading is important (i.e. mass α energy). Also the resistances associated with these electrodes were greatly reduced by a new cell design that almost eliminated the solution resistance. Different forms of carbon were tested including both powders and a fabric variety; the fabric electrodes exhibited a higher surface area, as well as much more mechanical stability. In the carbon powder work, it was found that the carbon Black Pearls 2000 was best for the specific capacitance (321 F/g) and it was optimized (higher specific capacitance, lower resistance) by the addition of 1% Nafion, while the total capacitance was optimized by a combination of 5% Teflon and 5% Nafion.

ACKNOWLEDGEMENTS

First and most importantly I would like to thank my supervisor Dr. Peter Pickup who provided a lot of help, both in physical (demonstrating how to correctly perform a procedure) and mental (in figuring out the best way to tackle a certain objective) aspect of the project. I would also like to thank the entire Pickup group (past and present), in particular Xiarong Liu, Aaron Rowe and Wanda Aylward for various help, advice and friendship around the lab. I would also like to thank the staff and faculty that I came in contact with while studying, in particular Viola Martin, Mary Flinn and Teresa Toope for their help with many of the procedures a student must go through, and the two other members of my supervisory committee, Dr. Bob Helleur and Dr. Ray Poirier. I also have to point out that the machine shop was very helpful in cell construction and maintenance. I would like to thank both The Department of National Defence and Memorial University of Newfoundland for making this project possible. Finally I would like to thank family and friends for their continuing support.

TABLE OF CONTENTS

List of Figures

List of Tables

List of Abbreviations

Abbreviation	Meaning
ΔH	Enthalpy Change
ΔS	Entropy Change
ΔG	Gibbs Free Energy Change
ΔV	Potential Change
I	Current
E	Energy
C	Capacitance
Cs	Specific Capacitance
R	Resistance
CFP	Carbon Fibre Paper
AC	Alternating Current
VCB	Vulcan Carbon Black
CV	Cyclic Voltammagram
IS	Impedance Spectroscopy
BP	Black Pearls
CF	Carbon Fabric
SG	Sol-Gel
TMOS	Tetramethylorthosilicate

SEM	Scanning Electron Microscope
RE	Reference Electrode
CE	Counter Electrode
WE	Working Electrode

Chapter 1: INTRODUCTION

1.1 ELECTROCHEMICAL FUNDAMENTALS

Electrochemistry is an important discipline in the chemical field with current and future applications for industrial as well as theoretical uses. With the current demand for energy, unique/different power sources must be implemented. This is an important discipline in the energy production field and due mainly to perceived environmental factors, is becoming more important every day.

1.2 CHEMISTRY AND ELECTRICITY

Chemistry is intrinsically linked to electricity; the very definition of electricity displays how important the concept of electron flow is. The two types of charge, positive and negative, are both quantized in magnitude with a charge of a single electron, that can be defined simply as e having a positive or negative value. As atoms contain both positively charged protons ($+e$) and negatively charged electrons ($-e$), they are the basis of all electricity.[1]

1.2.1 Thermodynamics

Thermodynamics can be defined as "the science of heat or energy flow in chemical reactions" and is the basis for electrochemistry. The first law of thermodynamics is usually simply known as the law of conservation of energy and states that energy can neither be created nor destroyed. This law may be somewhat misleading as it refers to the entire universe not only the small system in question. Take for example

a combustion engine in an automobile; it gains energy as it changes the hydrocarbons of gasoline into water and carbon dioxide. These two oxides are then distributed within the Earth's atmosphere; while they are lower in energy than the hydrocarbons they came from, the energy is balanced out by the combustion energy used to power the engine. The second law of thermodynamics states that in every process where work is performed a fraction of the energy is turned to heat that is either given off into the environment or passed on to other components of the same system. It may not be obvious that this has been done as some of the heat energy is used to energetically change the velocity of molecules in the system. The efficiency (i.e. fraction of useful work) is a function of temperature, as in the equation $Eff = 1 - T_1/T_2$ where Eff is the efficiency, T_1 is the temperature the process finishes at while T_2 is the temperature the predecessor starts at. As can be seen, in order to get 100% efficiency T_1 must equal 0 K or T_2 must equal infinity; this concept will be useful in describing why supercapacitors are useful as compared with traditional combustion engines. The third and final law of thermodynamics involves crystal structure and is not particularly relevant here.

Some processes/reactions occur spontaneously, i.e. they require no energy input in order to occur. Two main factors affecting the spontaneity must be defined; first we have *enthalpy change* (ΔH) the amount of heat energy transferred during a reaction; second the *entropy change* (ΔS) is the change in the measure of disorder a system undergoes. Both ΔH and ΔS help determine whether or not a reaction will proceed spontaneously. They are related to the reaction energetics in the equation for *Gibbs free energy change* (ΔG). It is this metric that determines if a reaction will be *spontaneous* (releases energy) or *non-spontaneous* (requires energy).[2] Conveniently, most of the

physical processes taking place can be measured in terms of enthalpy and entropy changes thus determining the change in free energy (as previously defined). The exact relationship is given by the equation: $\Delta G = \Delta H - T \bullet \Delta S$. A galvanic electrochemical cell can generate electricity spontaneously while a process known as electrolysis can use this electricity unspontaneously.[1]

1.2.2 Currents, Kinetics and Rate Equations

To begin with, the *current* (I) is defined as "the amount of charge passed in an electrical circuit per unit time"; it should be mentioned that electrochemical rates are measured in terms of I or as current densities (i), which is simply I divided by the area so it is the current per unit area, i.e. $i = A/m^2$ (or $/cm^2$ as it is in most cases). This is a very important measurement for electrodes which are highly porous and/or possess high surface-area. The kinetics for an electrochemical system are distinct from most chemical interfaces in that they are "dependent on the potential of the electrode". This characteristic is then usually compared with that of a reference electrode in the same electrolyte solution (a medium through which electrons or ions can flow unimpeded).[3,4] The chemical reaction rate is usually defined as how fast it proceeds.[5,6] Furthermore the rate of the reaction depends on the concentration of the reactants, as well as such factors as the pressure, temperature, and the volume the reaction takes place in.[2,6]

1.3 ELECTROCHEMICAL THEORY FOR SUPERCAPACITORS

The study of one of the most useful types of capacitors, supercapacitors, has become a significant and technologically demanding field.[7] Electrochemical capacitors exhibit a major advantage over classical capacitors; they exhibit 10^6 times the capacitance. Supercapacitors are usually constructed using activated carbons or high surface area RuO_2 as electrode materials with sulphuric acid or a tetraalkylammonium salt in acetonitrile solution acting as an electrolyte.[8,9] Because of apparent high operating power densities, as well as required technology for new engines of electric vehicles with miniscule amounts of hazardous emissions the need for supercapacitors is obvious. But compared with the already well known characteristics of batteries, a supercapacitor usually demonstrates a much lower energy density and a much higher rate of self-discharge. Because of this supercapacitors cannot replace batteries in commercial or industrial applications, but rather can be used to compliment them. The rapid charging and discharging of supercapacitors means batteries can be used to charge them and thus battery-supercapacitor hybrid systems are very applicable and desirable.[10] Another attribute supercapacitors possess is that they are usually constructed from relatively inexpensive materials, especially when they make use of aqueous electrolytes.[11]

1.3.1 Energy Storage Systems

Energy is of great concern in today's society; both its use and storage are requirements of any modern technological society. Electric energy storage can be achieved in two radically diverse ways. In the first method (*Faradaic*) energy is stored as in batteries, where electrons are transferred to or from an electrochemically active species,

thus creating a potential difference and the ability to generate energy. In the case of a battery this potential difference is generated at the interfaces of the negative anode and the positive cathode with the electrolyte. In the second method of energy storage (*non-Faradaic*), energy is stored more directly in an electrostatic way, as in the case of a capacitor where one plate is positively charged and the other plate is negatively charged.[3]

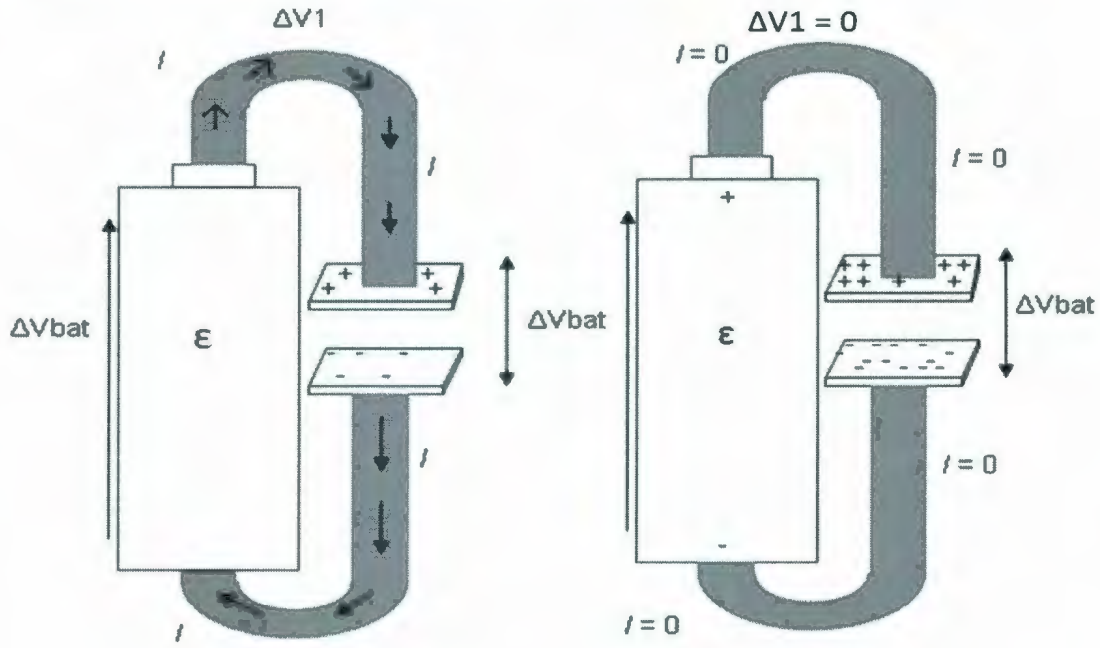
1.3.2 Faradaic and Non-Faradaic Supercapacitors and Pseudocapacitance

There are some major differences between the mechanisms involved in Faradaic and non-Faradaic supercapacitors in how they amass electricity. For double layer supercapacitors the charge storage is non-Faradaic, and in an ideal case no electron transfer occurs across the electrode interfaces; thus, electrostatic processes dominate. The type of energy storage exhibited by batteries and redox supercapacitors is Faradaic and does involve electron transfer across the double layers, and thus changes in oxidation state which change an electrochemically active species. There can be situations where both processes participate as part of the overall mechanism. When this occurs a continuous function of change in the charge (Δq) versus change in potential (ΔV) is observed, and this is known as *pseudocapacitance*. This is Faradaic in origin as it involves the passage of charge across the double layer, but unlike in a battery, it can be treated as a capacitance.[3] There is a unique thermodynamic relationship between the difference in charge acceptance and change of potential. The derivative dq/dV can be measured through various electrochemical techniques and can be substituted for the capacitance.

1.4 CAPACITANCE

Capacitance is measured in units of farads (F) and measures the quantity of charge a material can store through the equation C = Q/V where C is the capacitance, Q is the charge in coulombs (C) and V is the potential measured in Volts (V). While opposite charges attract, and the two oppositely charged plates of a capacitor attract one another, these plates don't instinctively discharge because the charges are unable to leap from one plate to the other. A linking wire can discharge the capacitor by way of creating a pathway for electrons to travel along in order for them to reach the oppositely charged particles, thus creating an electrical current, as can be seen in figure 1.1.[1, 12]

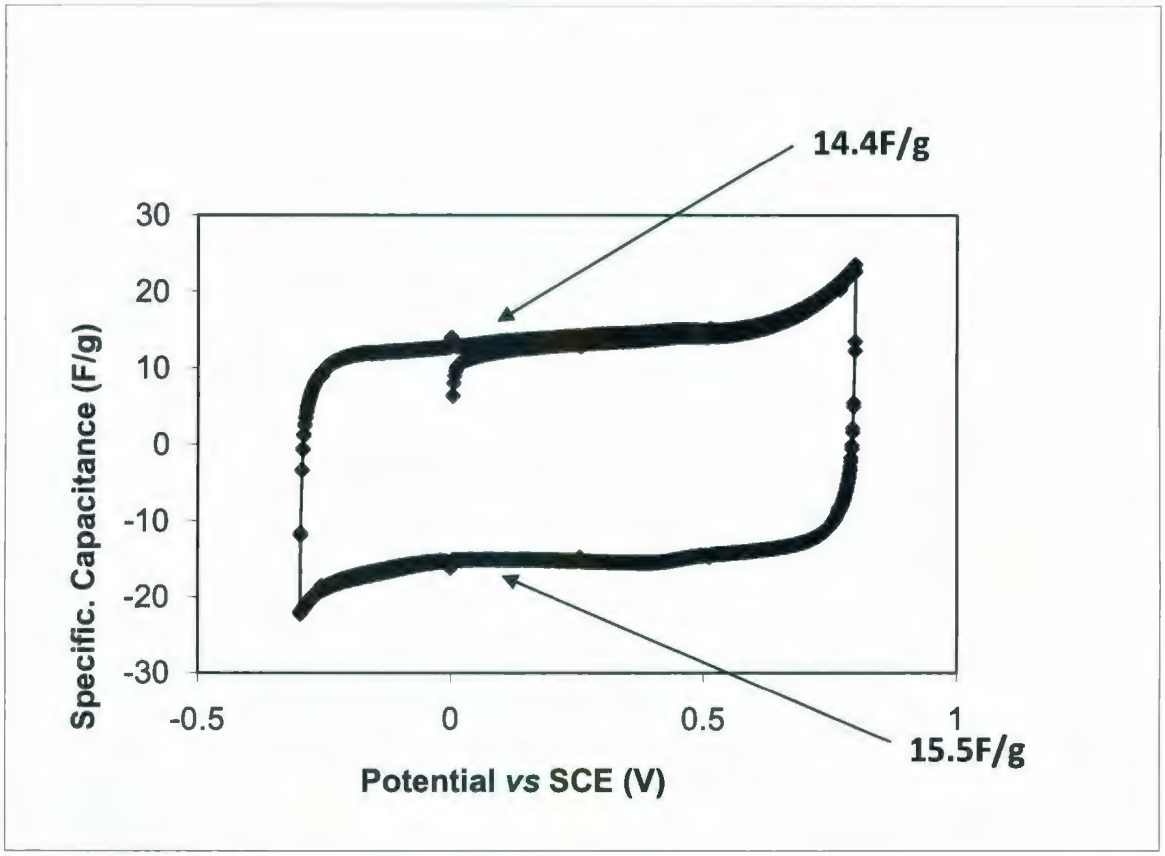
Figure 1.1 A schematic of a capacitor going from an uncharged to a charged state, where *I* is the current, ΔV_{bat} is the potential difference in the battery, ΔV_1 is the potential difference between the battery and the positively charged plate. In the 2nd case $\Delta V1 = 0$, and thus no current is flowing ($I = 0$) [12]



1.4.1 Measurement of Capacitance in Electrochemical Systems by Cyclic Voltammetry

Cyclic voltammetry is usually used to find the capacitance of a material in an electrochemical system. A controlled potential is applied to the material in an electrochemical cell and the resulting Faradaic and charging currents are measured as a function of this known variable potential. The scan begins at a selected initial potential value up until a programmed potential value. Charging of the electrodes double-layer occurs and specific Faradaic processes (i.e. oxidation) may occur within this range. The reverse scan, back to the initial potential reverses these processes (i.e. reduction). So this cyclic scan can give an estimate of redox potentials as well as providing information about the electrodes' stability and the electron transfer interaction. This process makes use of a working, reference, and counter electrode as well as an electrolyte that allows for ion passage. In a cyclic voltammagram, the current generated is plotted against potential used (I versus E curve). The I values can be converted into capacitance (C) units (F) by dividing by the scan speed (υ). Subsequent division by the mass of the electrode provides the specific capacitance in F g^{-1}. A typical plot for a carbon electrode, which mainly exhibits a double-layer capacitance, is shown in figure 1.2.[3]

Figure 1.2: A typical cyclic voltammagram showing the specific capacitance of a carbon electrode. The specific capacitance is calculated from the average of the Cs (F/g) value above the starting voltage (0.3 V in this case) and the negative of the Cs (F/g) value below the starting voltage. ((14.4 F/g + 15.5 F/g)/2 = 15.0 F/g)

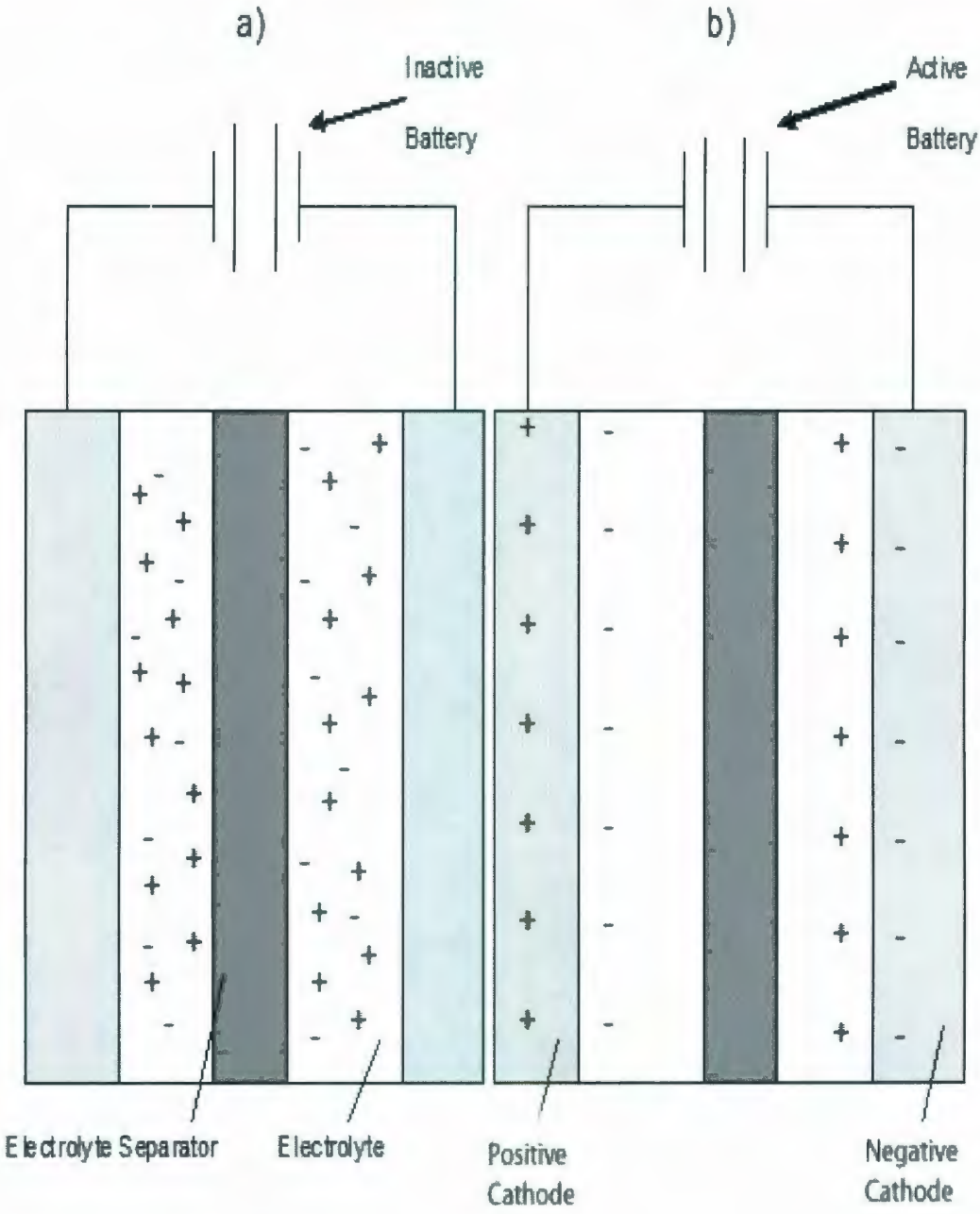


1.4.2. Electrochemical Double Layer Capacitance

The term for an interface containing oriented dipoles and charged particles is known as "the electric double layer" (EDL). This term however is usually made more specific in electrochemistry in that it is used to describe the interface between an electrode and the electrolyte.[10] While ordinary capacitors have an exceedingly low capacity for charge storage, unless they themselves are large (i.e. they have a rather small charge to mass ratio), if the electrolyte/electrode interface is charged it will exhibit double layers having capacitances of 16-50 $\mu F\ cm^{-2}$. A small value; however, with adequately large accessible electrode areas that can be met with high surface area carbon powders and felts, very large double-layer capacitances having orders of magnitude between 10 and 100 F/g have been achieved. It is partly this realization that has lead to the relatively new field of supercapacitors, also known as electrochemical capacitors, ultracapacitors or electrochemical double layer capacitors. This research has been flourishing and supercapacitors are now used as energy storage devices to compliment batteries in power output.[15, 1]

In supercapacitors, an electric double layer occurs at each electrode and charge can be stored at each electrode/electrolyte interface. Charge flow between the electrodes is driven by relaxation to the lowest ΔG value (as previously defined) possible. Since in an EDL the amount of capacitance depends on each of the two layers, the total capacitance of the cell (C_{cell}) is found by the following formula: $1/C_{cell} = 1/C_1 + 1/C_2$ where C_1 and C_2 represent the capacitances of layer 1 and 2, respectively. A simple schematic can be seen in figure 1.3 [4,16]

Figure 1.3 A diagram of a double layer capacitor showing how charge is stored. [4]



Because the charging of a double layer supercapacitor involves no phase or chemical change, (as opposed to batteries) they can be charged/discharged an extraordinary number of times, usually between 10^5 and 10^6 times. It is this characteristic that makes the processes powering the supercapacitor highly reversible. In an ideal supercapacitor, the cyclic voltammetry performed on it, in which a cyclic voltammagram is produced, will show almost mirror image charging and discharging components of the scan. In batteries, since the processes are usually less reversible, the components of the CV for charging and discharging can have major differences. It is this major difference which makes capacitor electrical storage systems preferred over their battery counterparts. Many opportunities come up where the complimentary action of batteries and supercapacitor is favoured due to the discharge/charge behaviour of the supercapacitor and the fact that while supercapacitors have increased energy densities relative to traditional capacitors, batteries are still needed to supplement the rather low peak power densities of the capacitors.[1,16,17]

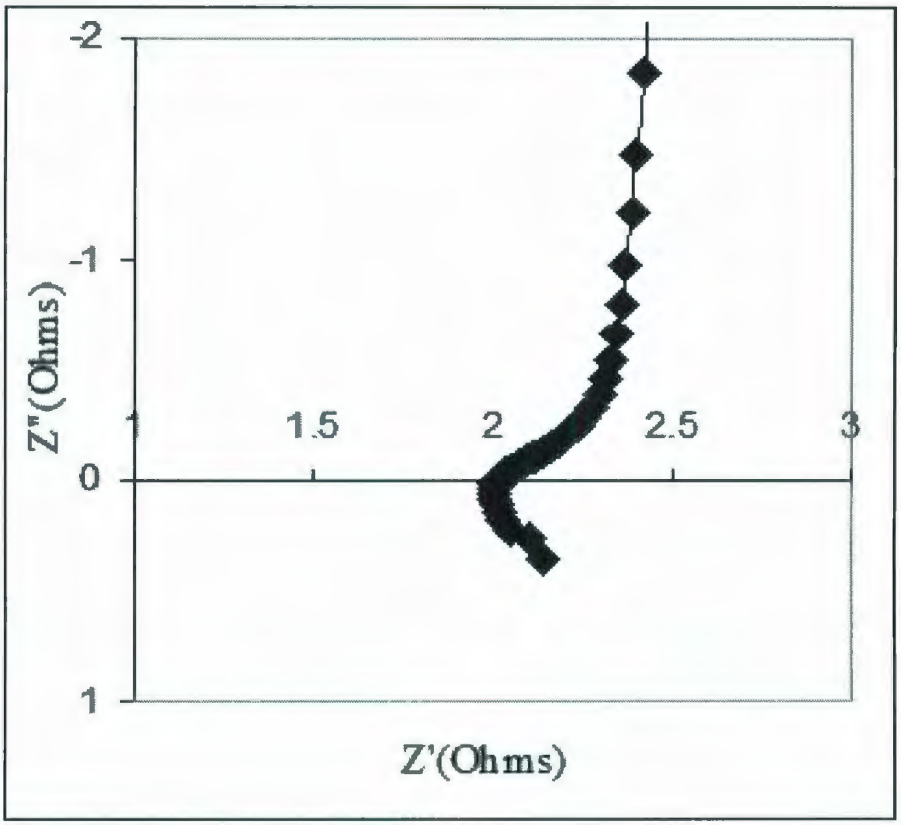
1.5 RESISTANCE AND IMPEDANCE SPECTROSCOPY

Resistance (R) is the ability of a circuit element to resist the flow of electrical current and is measured in units of Ohms (Ω). It provides a measure of the forces that hinder the flow of electrons. It is mathematically defined as R=E/I.

All materials have a natural resistance associated with them, however small it may be, and a conductor with no resistance has never been made. Materials with a higher resistance necessitate the need for a higher potential (voltage); thus, it is desired to use a conductor with a very low resistance. Resistance however, can be a necessary property

as it generates the energy that electricity uses to power everyday products, such as light bulbs and heaters.[12] Resistance (strictly impedance) is a function of frequency, so low frequency measurements differ greatly from their high frequency counterparts. Resistance in an electrochemical cell is usually characterized by impedance spectroscopy which applies a potential (usually AC) to the cell and measures the current response. This signal is measured as a sinusoidal wave function and can be analyzed though a Fourier Series.[12] The results can be represented as a Nyquist plot which shows the imaginary component of the impedance against the real component. From this plot (an example of which is shown in Figure 1.4) the resistance can be calculated from the following equation: $R = 3(R_{low} - R_{high})$, where R_{low} is the low frequency real component of impedance and R_{high} is the high frequency component. In the case shown in Fig. 1.4, $R_{high} = 2.02\ \Omega$ and $R_{low} = 2.31\ \Omega$, so $R = 0.87\ \Omega$

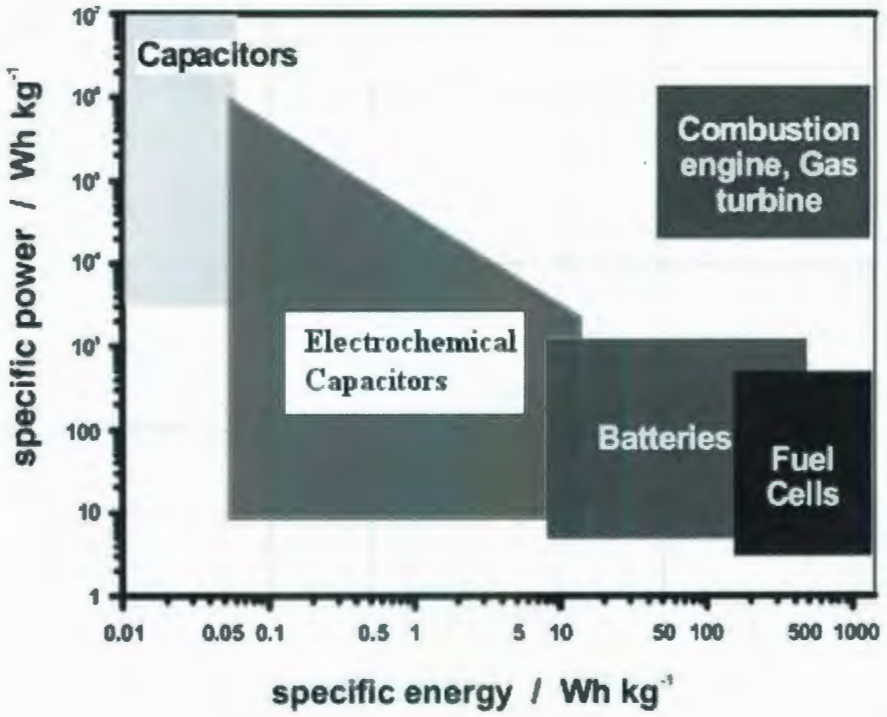
Figure 1.4: A typical Nyquist plot in which Z' is the real impedance and Z" is the imaginary impedance. R_{low} is the measurement where the vertical line meets the horizontal axis, similarly R_{high} is where the diagonal line meets the horizontal axis.



1.6 POWER AND ENERGY

A very notable and long-standing discussion in the engine industry has been about the relationship between the power and energy outputs of various machines. In particular the power density versus the energy density correlation was studied. In the battery field this relationship was greatly scrutinized as it is very important to both practical use and theoretical study. One common way in which these can be compared is through a Ragone plot; an example of which can be seen in figure 1.5. In this plot the power density is plotted versus the energy density.[11,13,14]

Figure 1.5: A Ragone plot showing the energy density versus the power density for various energy storage systems. [15]



1.7 ELECTROCHEMISTRY OF CARBON

The properties of carbons in electrodes for supercapacitors are very attractive, as they possess a comparatively low cost, wide potential range, easy surface reproducibility, high surface area, and prevalent availability. These are some reasons why carbon has been commonly used as a beneficial material in fuel cells. Because of some electrochemical advantages carbon has been found to possess (i.e. increased battery life, capacitance) and the diverse range of chemical and physical properties that are observed in different forms of carbon, it has become the most widely used electrode material in electrochemical

applications, including supercapacitors.[18] All kinds of carbonaceous materials can be used but of particular benefit in supercapacitors are active carbons. Active carbons are made from the combustion of an assortment of raw materials followed by an activation procedure. While the structure of the consequential active carbon relies on the activation agent and activation conditions, the qualities of the raw material greatly influence the characteristics of the product. Active carbons are especially useful because, along with having a large surface area they also possess slit-like micropores. It is the latter feature that determines their ability to be an excellent adsorbent. On the other hand, carbon blacks are usually obtained by thermal cracking of hydrocarbons in an oil furnace, by controlling certain features of this procedure the physical and chemical properties can be moulded to obtain the desired product.

To be useful as an electrode material carbon is usually combined with a specific binding polymer. Some popular examples of binding polymers being polyvinylfluoride, polyvinylchloride, Nafion and Teflon.[3,18] These allow the carbon powder to be made into a compact pellet so that there is good electrical contact between all the carbon particles in the electrode. These binders are usually water soluble and organic in nature.[18] The accumulation of the polymer must be minimized as it increases the resistivity of the electrode by blocking some of the pores. Conversely, special care must also be taken to ensure that enough polymer has been added to provide physical stability. Usually amounts vary between 5 and 10% by weight.

Carbon electrodes in aqueous media possess a practical potential range that is usually limited by the background oxidation/reduction of the electrolyte. The two main processes that affect the potential range are hydrogen and oxygen evolution.[13]

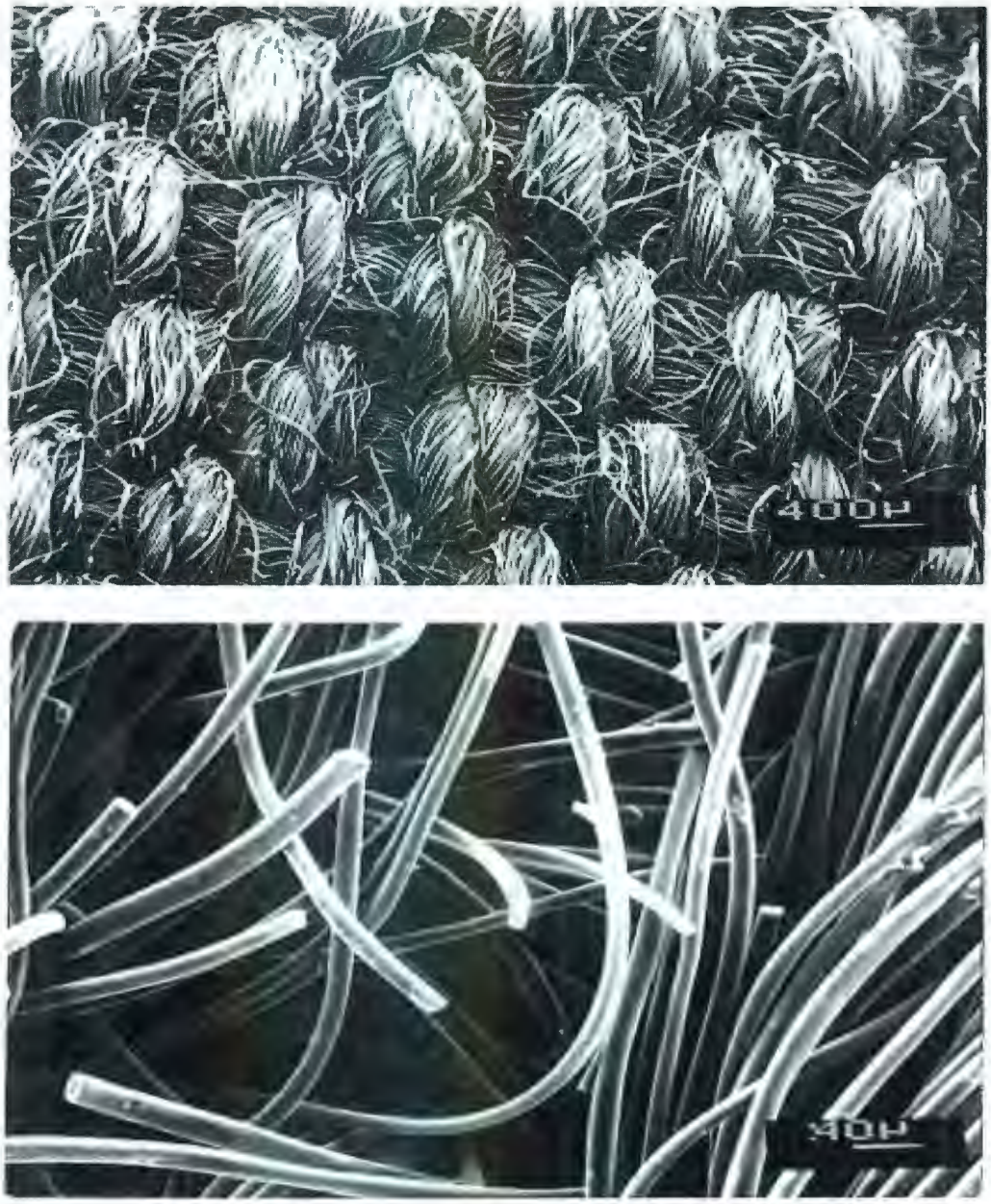
1.7.1 Different Structural Forms of Carbon

Carbon naturally exists in two distinct bonding styles. In the diamond form each carbon atom is bonded to four neighbours having a tetrahedral geometry giving it the properties of an insulator. In graphite, the atoms are arranged in weakly bound hexagonal sheets. Carbon Blacks are similar to graphite structurally but are created by combustion of hydrocarbons and possess electrochemically desirable properties. They can be simply described structurally as near graphite like spheres. Carbon in this form gives the best capacitance, mainly because of the orientation of the bonds and their related bond strengths.[3, 19]

1.7.2 Spectrocarb

The official name of this high surface area carbon felt is Spectrocarb 2225 (for more information see table 2.3). It exhibits much more stability (mechanical integrity) and a higher surface area than the afore mentioned carbon blacks.[5,20] Many different materials including yarns, long filaments and cloths (both knitted and woven, see figure 1.6) are used in the manufacture of this.[17]

Figure 1.6. Scanning electron micrographs of Spectrocarb. The size markers represent 40 and 400 μm, respectively.



1.8 USES OF SUPERCAPACITORS

Many battery-powered devices have power needs that vary greatly as their mode of operation changes. Some need high-current power pulses that may be difficult or impossible for batteries to supply without increasing the risk of performance failures, reduced operational life, or even premature battery failures. The problem is that batteries have high internal resistances (such as ESR) too large to continue to consistently deliver high-power pulses. Devices that would require high-power pulses include:

- GPS tracking systems
- Bluetooth communications devices
- LED safety flashers
- Bar-code equipment
- Remote-control systems
- Medical equipment
- Alarm and security systems
- Portable music players and other audio amplifiers

It is well known that adding supercapacitors in parallel with the source battery can help supply power during these pulses. As supercapacitors have become more cost effective, they are used increasingly in this role.[21]

1.9 OBJECTIVES OF THIS WORK

The main objective of this work was to develop carbon based electrodes for use in supercapacitors. Using different forms of carbon, different testing methods as well as different binding polymers it was foreseen that carbon electrodes with better characteristics than those currently published in the literature could be achieved. In particular, the development and study of supercapacitors based on Spectrocarb® fabric was targeted, since this appeared to have very suitable characteristics relative to carbon blacks.

References:

1. Knight R.D. *Physics: For Scientists And Engineers,* Pearson Educational Inc.; San Francisco, California (2004)
2. Koltz J.C., Purcell P.F. *Chemistry and Chemical Reactivity* Saunders College Publishing; Montreal, Quebec (1991)
3. Conway, B. E. *Electrochemical Supercapacitors Scientific Fundamental and Technological Applications.* Kluwer Academic / Plenum Publishers, Boston, Massachusetts (1999)
4. Brown T.L., LeMay H.E., Bursten B.E. *Chemistry: The Central Science*: 10th edition: Pearson Prentice Hall; Upper Saddle River, New Jersey (2006)
5. Berg J. M., Tymczko L. J. and Stryer L. *Biochemistry.* W.H. Freeman and Company, New York, New York (2002)
6. Chang R; *Chemistry.* McGraw-Hill, Boston, Massachusetts (1998)
7. Pandolfo A.G., Hollenkamp A. F. *J. Power Sources,* **157**, 1 (2006)
8. Saragapani S., Tilak B.V., Chen C-P, *J. Electrchem. Soc.* **143**, 11 (1996)
9. Allahyarov, E., Taylor, P.L. *J. Chem. Phys.* **127**, 15 (2007)
10. Burk, A. J., *J. Power Sources*, **91**, 37 (2000)
11. Brodd, R., Winter, M. *Chem. Rev.*, **4245**, 104 (2004)
12. Wang J.; A*nalytical Electrochemistry.* Whiley-VCH: A John Whiley & Sons, Inc.; Hoboken, New Jersey (2006)
13. Niu J., Pell W. G. and Conway B. E., *J. Power Sources,* **156**, 2 (2006)
14. Dicks A.L., *J. Power Sources*, **156**, 2 (2006).

15. Laidler K.J, Meiser J.H.; PHYSICAL CHEMISTRY: 3rd Edition. Houghton Mifflin Company, Boston (1999)

16. Guggenhiem, E. A., *J. Chem. Phys.* **253**, 13 (1945)

17. Kruk M, Jaroniec M, Bereznitski Y., *J. Colloid Interface Sci.* **182**, 1 (1996)

18. http://www.spectracorp.org/spectracarb2225.html

19. Moseley P.T., Nelson R.F. and Hollenkamp A.F., *J. Power Sources,* **157**, 1 (2006).

20. Grahme D. C., Chemical Reviews, 41, 441 (1947).

21. http://www2.electronicproducts.com/Supercapacitors_evolve_to_meet _ market_needs -article-fapo_illinoisCapacitor_dec2009-html.aspx

Chapter 2: EXPERIMENTAL CHARACTERISTICS

2.1. CHEMICALS AND MATERIALS

In the Table 2.1 chemicals and materials used in this work are listed, with the source from which they were obtained (purchased) and their core utilization. All materials were used as received, unless otherwise stated.

Table 2.1: List of products used

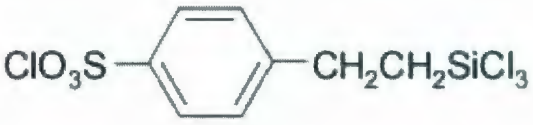
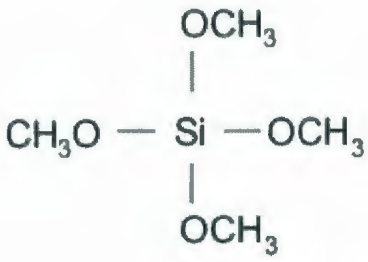
Product	Source	General Use
Vulcan-XC72	Cabot Corporation	Electrode Material
Black Pearls 2000	Cabot Corporation	Electrode Material
Norit SX Ultra	Norit Americas Inc.	Electrode Material
Ketjenblack ED600JD	Akzo Nobel	Electrode Material
Spectrocarb 2225	Engineered Fibers Technology	Electrode Material
Carbon Fibre Paper (TGPH060)	Fuel Cell Store	Electrode Material
Celgard 3400 Microporous Membrane	Celgard, LLC	Separator
Nafion (115 sheet)	Aldrich Chemical Company	Separator
Nafion (liquid) (5wt %)	Aldrich Chemical Company	Binder
Teflon (liquid) (60 wt %)	Aldrich Chemical Company	Binder
H_2SO_4	Fisher-Scientific	Electrolyte
Acetonitrile (anhydrous) (99.8 %)	Sigma-Aldrich	Electrolyte
Dichloromethane (ACS Reagent grade)	ACP Chemicals	Electrode Material

2.2 ORMOSIL GEL

2.2.1 Ormosil Gel Description

An ormosil gel (Sol-Gel, SG) was used as a binder in some experiments. It was thought, with benzene groups and sulfonic acid functionality, that SG would be a very applicable binder for supercapacitor electrodes. The starting materials, the 2-(4-chlorosulfonylphenyl) ethyltrichlorosilane (silane) and the Tetramethylorthosilicate (TMOS), another component of the SG has the structure seen in tables 2.2A & 2.2B. respectively.[1,2]

Table 2.2: The structure of A) Silane and B) TMOS.

A) Structure of the silane	B) Structure of TMOS
	

2.2.2 Ormosil Gel Synthesis

The ormosil gel was made in a round bottom flask, containing a magnetic stirbar, which was thoroughly dried in a 90°C oven beforehand. A 0.6 ml sample of 50% silane in dichloromethane and 1.5 ml of 98% TMOS were transferred to the flask with the use

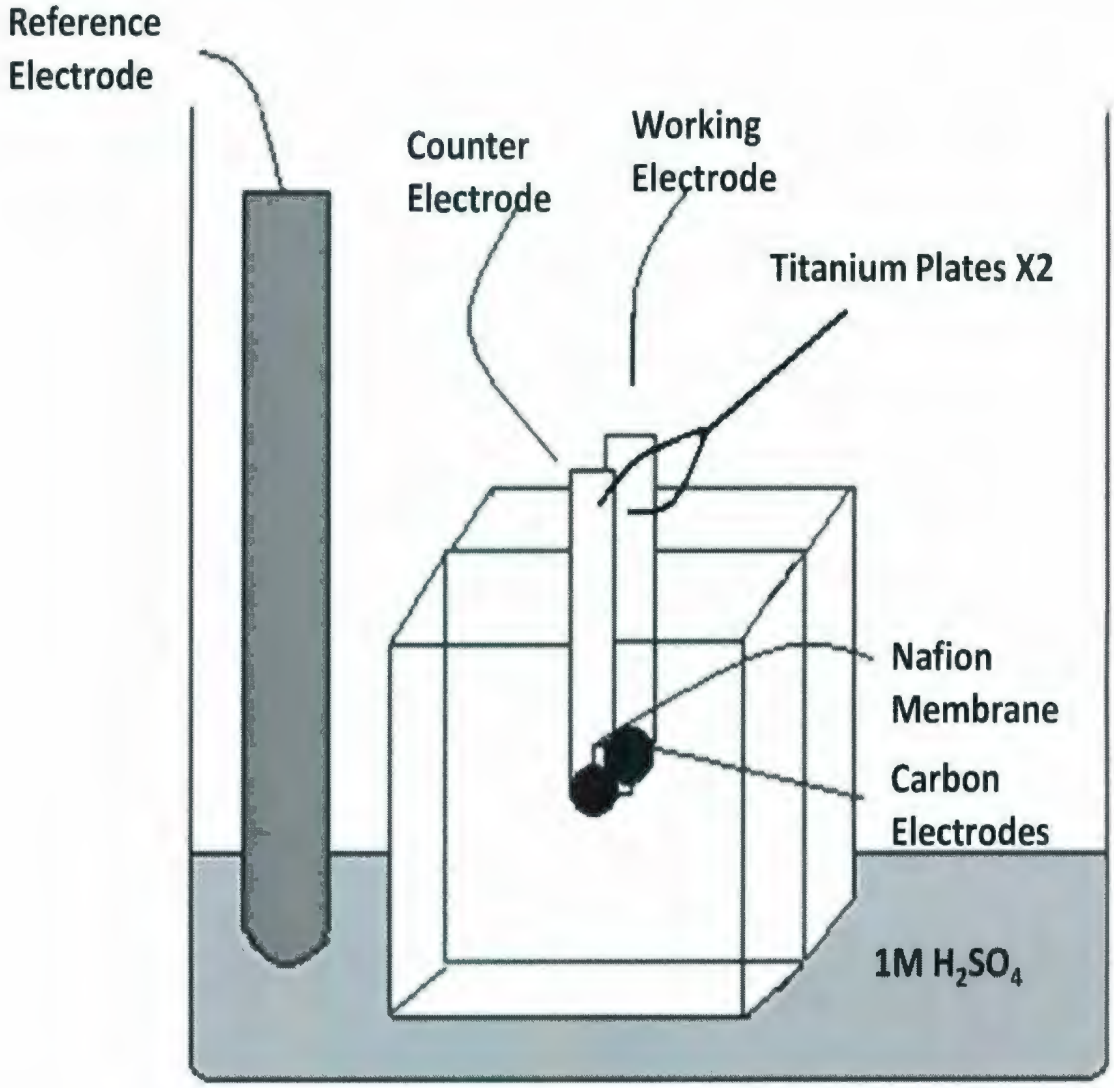
of a glass disposable volumetric pipette to maintain a dry environment for these reagents. After these had been added, the hydrous compounds (water, methanol and hydrochloric acid) were added to the silane and the TMOS and the resulting solution was then refluxed for 1½ hrs.[3] Upon cooling, the resulting sol gelled over a period (3-5) of days. Samples of the sol-gel were stored in a freezer until needed. If used within a few weeks, they were reasonably liquid when thawed, and would then gel within several days.

2.3 CHARACTERIZATION OF CARBON ELECTRODES

2.3.1 Methods

Most of the impedance spectra and cyclic voltammagrams in this study were generated in a sandwich style cell (see Ch. 3), in an electrolyte that consisted of 1M H_2SO_4 and using a calomel reference electrode (SCE). The working electrodes that were used in the cell were various high surface area carbons (see Table 2.1) deposited on a carbon fibre paper disk with an approximate surface area of 1 cm^2, which were then placed on titanium strips. This can be better visualized in figure 2.1.

Figure 2.1: A simple schematic of the sandwich style cell and how it is set up for electrochemical analyses.



Cyclic voltammagrams were collected using a Pine Instrument RDE4 Potentiostat. Impedance spectroscopy was performed using a Solartron 1286 Electrochemical Interface in combination with a Solartron 1250 Frequency Response Analyzer, and using ZPlot version 2.6b and Zview version 2.6b software.

2.3.2. Experimental Variables

There were some variables that were used in all experiments; the first of these being the scan speed. In initial experiments a scan speed of 100 mV/s was used in order to get fast results. However this scan speed produced significant internal resistance effects so a speed of 50 mV/s was substituted in some later tests.[4] Since this still caused underestimation of capacitance, the scan speed was lowered to 10 mV/s; this is the speed that was settled on. The scan speed is noted for each set of data.

The next variable is the potential. In all experiments performed in the 1M H_2SO_4 electrolyte the potential was varied from -0.300 to +0.800 V, while when acetonitrile was used the potential range was increased to -1.999 to +1.999 V. This is because of the fact that acetonitrile can be tested over a very large potential range without major oxidation due to the electrolyte. H_2SO_4 is oxidized at a much lower potential when compared with oxidation of acetonitrile.[5]

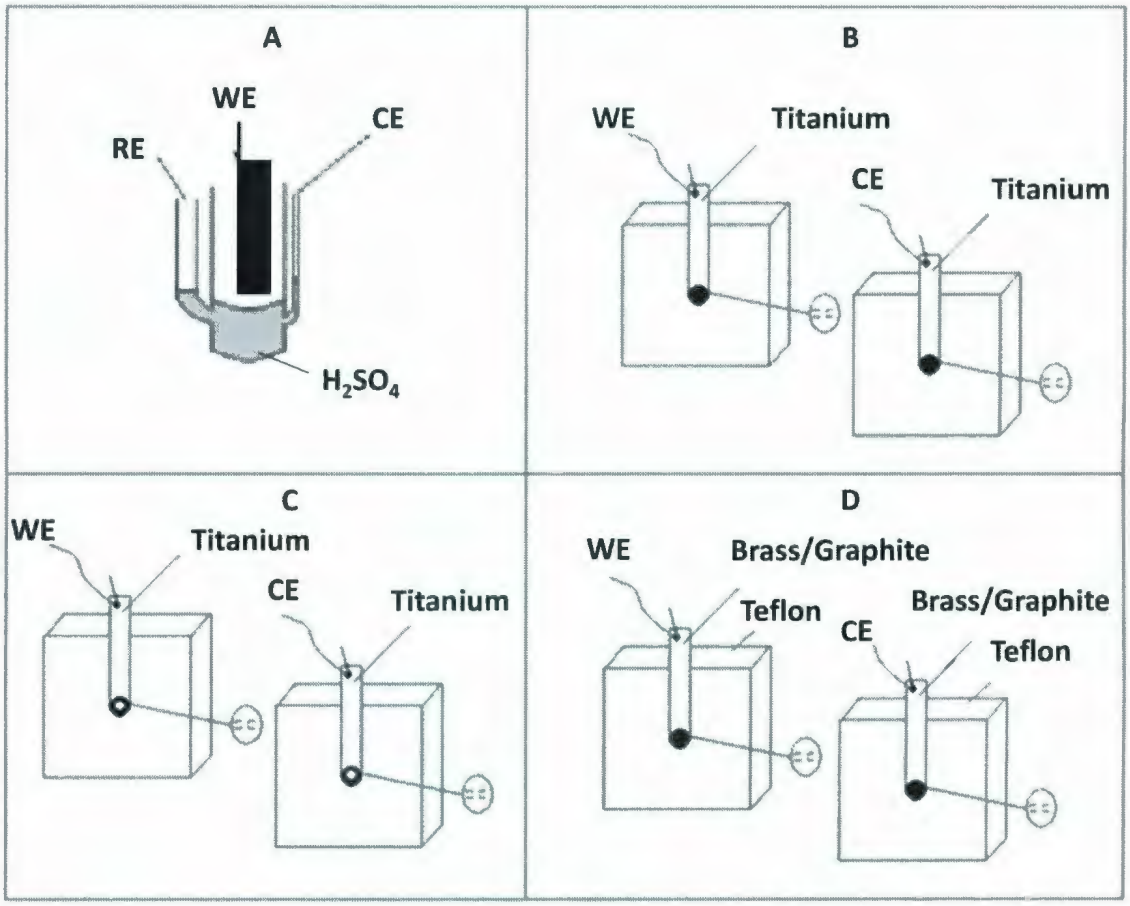
In impedance spectroscopy these factors do not apply directly; instead impedance has other factors that only apply to it. The first being potential; while a CV is run over a broad potential range, impedance spectroscopy only measures data at one predetermined potential. That is not to say impedance spectroscopy only provides a single data point, since data is collected over a range of frequencies. As can be seen (in Chapter 1 figure

1.3) an impedance spectrum is composed of a plethora of points. Because Nyquist plots represent capacitance and resistance as a function of frequency, the frequency range under which an electrode is tested is very important as both of these characteristics are calculated at each frequency response. So a larger frequency range leads to more accurate results.[6]

2.3.3 Cells Designed

A number of different cells were developed and used during this work, as displayed by figure 2.2 a-d. The original cell can be seen in figure 2.2a and consists of a hollow glass cylinder with three openings. This worked adequately but gave a large solution resistance (Rs),[7] so a new cell (seen in figure 2.2b) was fashioned. In this sandwich style cell the Rs was minimized, and the counter electrode used was another carbon electrode of comparable resistance and capacitance. In most cases, Spectrocarb was used due to its high specific capacitance and low resistance. It was found that the electrolyte soaked too slowly into most electrodes. In order to remedy this, a cell was made with 1 mm round holes on the outside of the cell on the two sides directly holding the electrodes. With this the H_2SO_4 was able to access the electrodes from the sides as well as the more delayed route from the bottom; this is depicted in figure 2.2c. Finally a cell was constructed similar to the last one only instead of the outer casing being made of a polyresin plastic it was made out of Teflon. This was only used in a few cases where instead of H_2SO_4 we used acetonitrile as the electrolyte. These cells were all placed in a beaker containing a small amount of H_2SO_4 (acetonitrile in figure 2.2d's case) and the reference electrode.

Figure 2.2 (A-D): Different cells designed for carbon electrodes: A = Original cylindrical cell, B = Sandwich style cell, C= Sandwich style cell with holes drilled, D = Sandwich style cell designed for use with acetonitrile; where *CC* stands for carbon electrode. *Note in B, C, and D the two halves of a cube are shown, the two are forced together with the CC in the middle.



2.3.4 Electrode Preparation

The Carbon Fibre Paper (CFP) was cut into disks for the sandwich cells (figure 2.4C-D), or strips for the cylindrical or conventional cell (figure 2.4A). Once the small, appropriate shaped disk/strip had been cut out of a much larger sheet, the carbon black mixture (specific carbon black, binder, isopropanol) was pressed into a certain area with a spatula. A ~1 cm^2 area was covered by the carbon mixture and the appropriate cell containing the disk/strip was assembled. This was connected to a potentiostat and either CV or IS was run on it.

2.3.5 Exceptions

There were a small number of cases in which instead of using 1 M H_2SO_4 as the electrolyte, a solution of 1 M Et_4NBF_4 in 99.8% acetonitrile was substituted. Also in a small number of cases a lugging capillary was used in the cell in order to achieve a more uniform potential distribution between the reference electrode and the working electrode. After the use of the lugging capillary proved unsuccessful, instead of using a reference electrode, the counter electrode was substituted so two of the three wires were connected to it, thus analyzing the electrode in supercapacitor (or 2-electrode) mode.

2.3.6 Different Carbons used for Electrodes

All of the electrodes used in this work were made of different forms of carbon. Generally small amounts of other chemicals were mixed in to improve electrochemical characteristics. The different types of carbon used for electrodes are listed in table 2.3.[1,4,8,9]

Table 2.3: Different types of carbon particles used in this work.

Type of Carbon	Surface Area (m^2/g)
Vulcan-XC72	250
Black Pearls 2000	1450
Norit SX Ultra	1320
Ketjenblack ED600JD	1400
Spectrocarb 2225*	2500

*** Spectrocarb was a carbon cloth, so the particles were all woven together making a fabric.**

2.3.7 Different Calculations used for the Analysis of Electrodes

In this study two different complex characteristics of the electrodes' were determined, that of the capacitance (or more frequently the specific capacitance) and the resistance. As previously mentioned in this chapter these are both computed using different instrumentation and thus different characteristics are revealed. First, for the capacitance a cyclic voltammagram reveals the current generated as it is plotted against potential used. The current values can be converted into capacitance by dividing by the scan speed; this is explained in more detail in chapter 1. The other major measure that is calculated is the internal resistance, a Nyquist plot which shows the imaginary component of the impedance against the real component, then some calculations using the frequency of different points on this graph are used to find the resistance (for exact numbers see chapter 1.5).

References:

1. Aylward, W. M. Pickup, P. G. *J. Solid State Electrochem.*; **8,** 10 (2004)
2. Mostafa, M. R. Abuelnader H. M., *Anafinad;* **50**, 446 (1993)
3. Kruk, M. Jaroniec, M. Bereznitski, Y., *J. Colloid Interface Sci.;* **182,** 1 (1996)
4. Liang, P. Huang, X. Fan, MZ., Cao, XX *Appl. Microbiol. Biotechnol.*; **77**, 3 (2007)
5. Stamenkovic, V. Markovic, N.M., Ross, P.N., *J. Electroanal. Chem.;* **500**, 1-2 (2001)
6. Conway, B. E., *Electrochemical Supercapacitors: Scientific Fundamental and Technological Applications. Kluwer* Academic / Plenum Publishers, Boston (1999)
7. Lee, G-J. Pyun, S. Kim, G-H., *J. Solid State Electrochem.*; **8,** 2 (2003)
8. Fujiwara N. Yamazaki S. Siroma Z. Ioroi T Yasuda K. Electrochem.Communications; 8, 5 (2006)
9. Valente Nabais J. M. Canário T. *et. al., J. Porous Mater.;* **14,** 2 (2007)

Chapter 3: CARBON POWDERS

3.1 INTRODUCTION

This project mainly focused on the electrochemical properties of carbon electrodes; for this research, carbon blacks were used most often because of their massive surface area and relatively low price. Many sources in the literature have successfully used carbon as electrodes[1-4] and they are very well suited to supercapacitors because of their physical and chemical properties. Resistivity/conductivity is of great concern in electrochemical applications, this data is greatly varied as many different structural forms of carbon exist. And as carbon is relatively inert it is ideal as it can be tested throughout a large potential window.[3,4] The main purpose of the work reported in this chapter was to develop high-quality experimental methods to compare and optimize the use Nafion and a sulphonated sol-gel as binders for carbon supercapacitor electrodes.

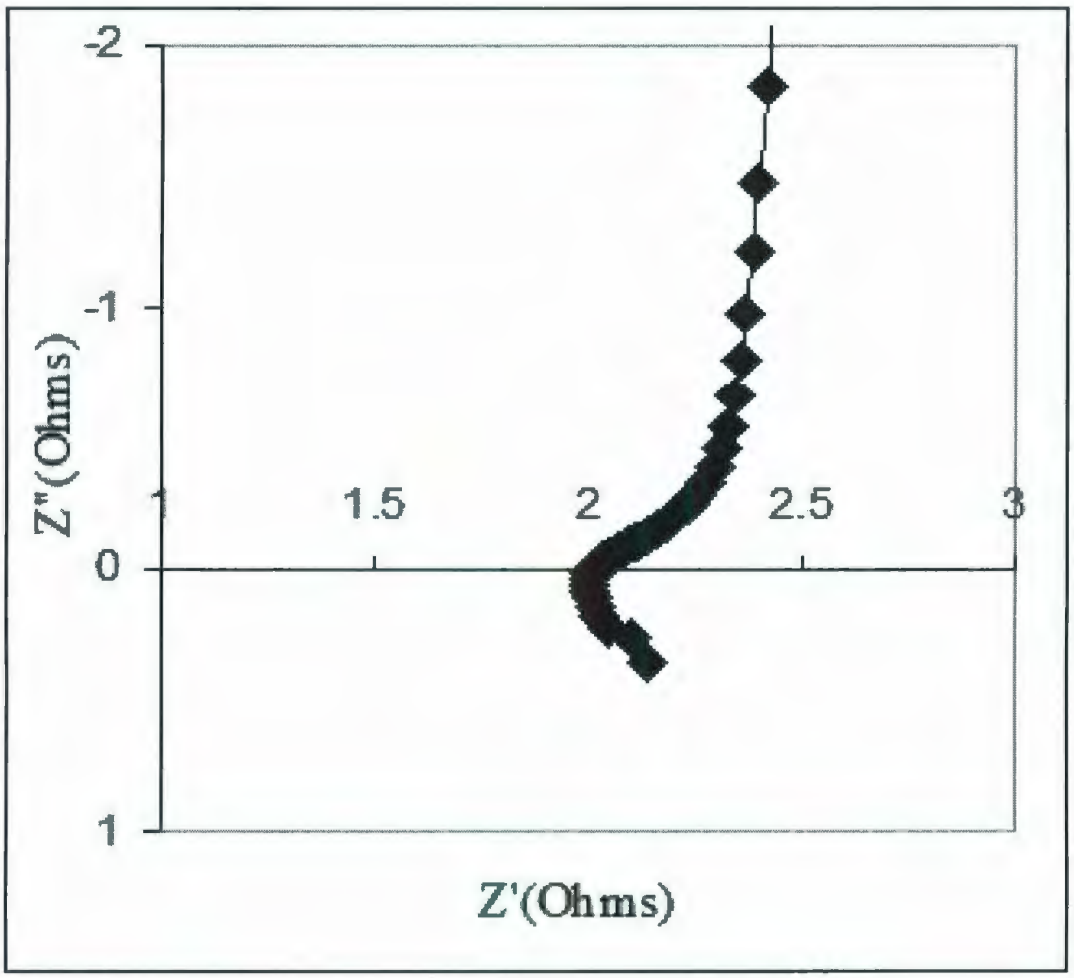
3.1.1. Experimental

The carbon powders were all tested by depositing them on a strip/disk (depending on the cell used) of carbon fibre paper (CFP) that was placed in an electrochemical cell containing a suitable electrolyte (H_2SO_4(aq) in most cases) and tested via cyclic voltammetry (CV) and impedance spectroscopy (IS). Details are provided in chapter 2 (2.3.4).

3.2 VULCAN-XC72

Vulcan-XC72 (VCB for Vulcan carbon black) is the carbon black employed with the lowest surface area (250 m^2/g), and was used for a small number of initial experiments to develop methodology for collecting both cyclic voltammagrams and impedance spectra. VCB is a powder and in order to keep the particles in close proximity with one another, 5 % (by mass) of the polymer binder Nafion was added; then a few ml of isopropanol were added and the resulting mixture was placed in an ultrasonic bath for ~5 min to produce a homogeneous suspension. This was then spread onto the CFP strip, where it was left to air dry (to remove isopropanol and solvents from the Nafion solution). After the strips had thoroughly dried they were massed and placed in a conventional 3-electrode glass cell (depicted in figure 2.2). The electrode was then tested by IS at a potential of 0.3 V and a minimum frequency of 0.1 Hz. A sample Nyquist plot, generated by Zview, of an electrode made from VCB is shown in figure 3.1. In this glass cell an average resistance (most of this was due to uncompensated solution resistance) of 0.92 Ω was found (by the method explained in section 1.5).

Figure 3.1: A typical impedance plot for an electrode containing VCB (0.8 mg) and Nafion in 1 M H_2SO_4 showing the imaginary impedance versus the real impedance.



Cyclic voltammetry was performed on similar electrodes using a scan speed of 100 mV/s, and a potential range of -0.300 V to +0.800 V. Figure 3.2 shows some typical CVs of VCB electrodes. Peak specific capacitance (Cs) values for these and other electrodes are listed in table 3.1. As can be seen from this table, results tend to vary significantly. The average peak Cs was 17.2 ± 3.9 F/g. The most commonly accepted

literature values range from 12 – 13.7 F/g, but it was not mentioned whether or not these values were obtained using an efficient amount of binder. [5,6]

Figure 3.2: Cyclic voltammagrams (100 mV/s) of 3 similar VCB electrodes having peak specific capacitances of 13 F/g to 17 F/g.

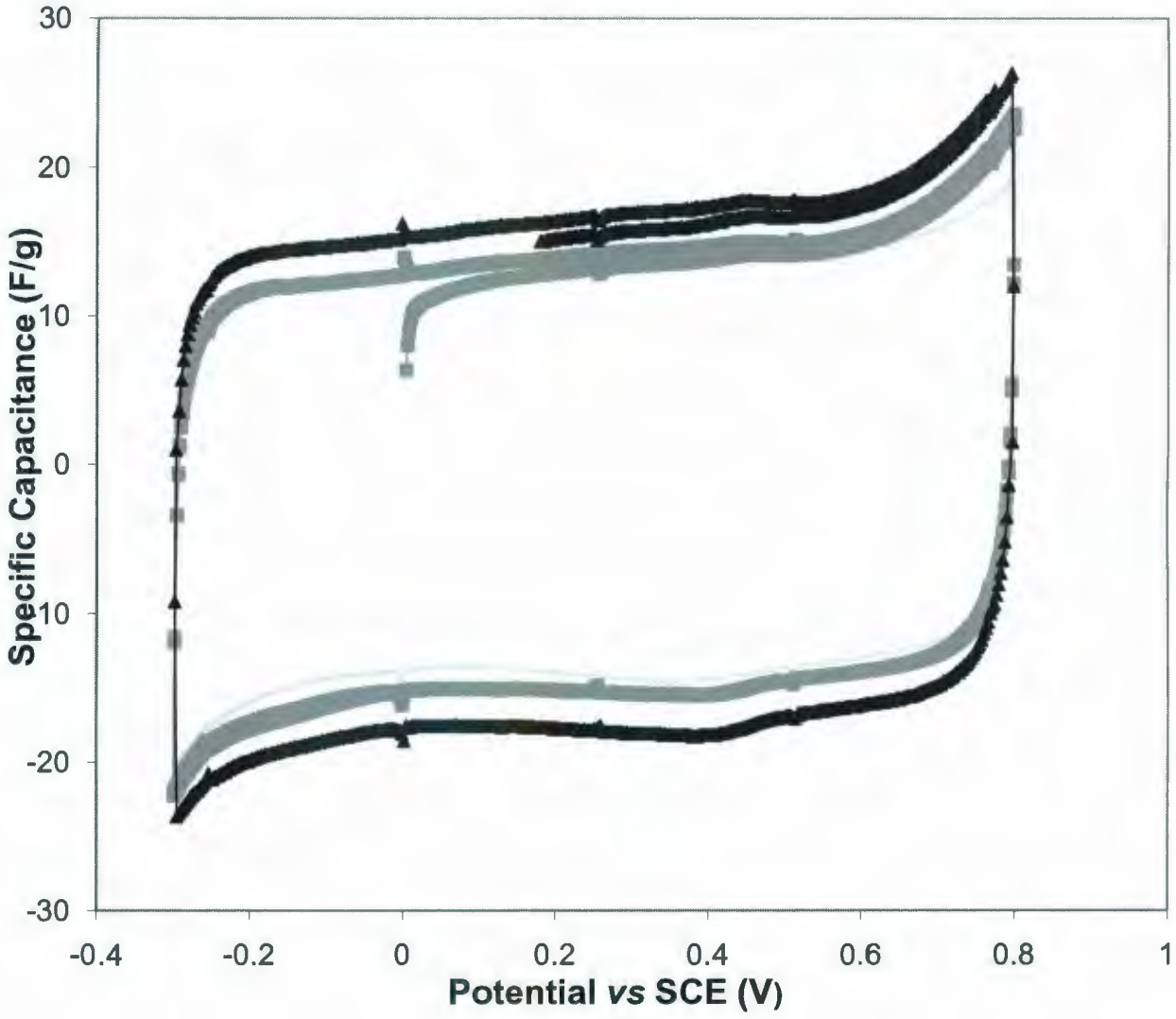


Table 3.1: CV results obtained when testing VCB in the conventional cell.

Loading (mg)	Specific Capacitance (F/g)
2.0	14.5
2.1	19.5
2.3	16.1
2.5	26.8
Average: 2.2	Average: 19.2

3.3 BLACK PEARLS 2000

While the VCB had a low surface area, significant capacitance and low resistance values were found. Black Pearls 2000 (BP) is a carbon black powder with a higher surface area of 1450 m^2/g.[7] It was realized early on that the capacitances achieved with BP were much higher than corresponding results with VCB. The BP was initially tested in the conventional glass cell, but a sandwich style cell (fig. 2c) was used in most work. The BP was not only tested for capacitance, but it was used for such things as evaluating the effectiveness of new cell designs; by comparing results with those of the original cell any difference could be determined. As BP exhibited a much higher capacitance, differences were seen easier than they were using comparable tests on the VCB. Another test that was bestowed on the BP was of how the capacitance changed with the potential applied to it. And while it was the VCB that was originally used to evaluate the use of Nafion as a binder, BP was used to optimize the % of it used in the carbon paste (a mixture made up of BP + Nafion + isopropanol). BP was also used to test the ormosil's (SG) effect on the capacitance. Finally the BP was the carbon used most in efforts to increase mass loadings.

3.3.1 Black Pearls in the Conventional Cell

Similar to the VCB, the BP suspension was made up of a higher surface area: (1450 m^2/g) carbon, 1% Nafion (normally) and a few ml of isopropanol. This mixture was not homogeneous, and even after sonication the solid BP was not evenly dispersed throughout the mixture. A spatula was dipped into the mixture and used to collect the thicker paste-like component; this was then mashed into the carbon fibre paper strip.

By the addition of Nafion binder to the VCB the Cs increased, as the particles were held together better. The same behavioural results were expected with the BP. Four BP electrodes were prepared with 5% Nafion as a binder and these were tested by CV giving rise to table 3.2. An average Cs of 107.8 +/- 15.8 F/g was obtained.

Table 3.2: Cs results from 4 electrodes that used 5% Nafion as a binder

Electrode #	Cs (F/g)
1	116
2	104
3	119
4	92

These same 4 electrodes were tested by IS, and an average Cs of 97.5 +/- 11.1 F/g was obtained. The CVs for these electrodes are shown in figure 3.3A, while an IS of a relevant electrode is shown in figure 3.3B.

Figure 3.3A: CVs of 4 electrodes containing BP + 5% Nafion

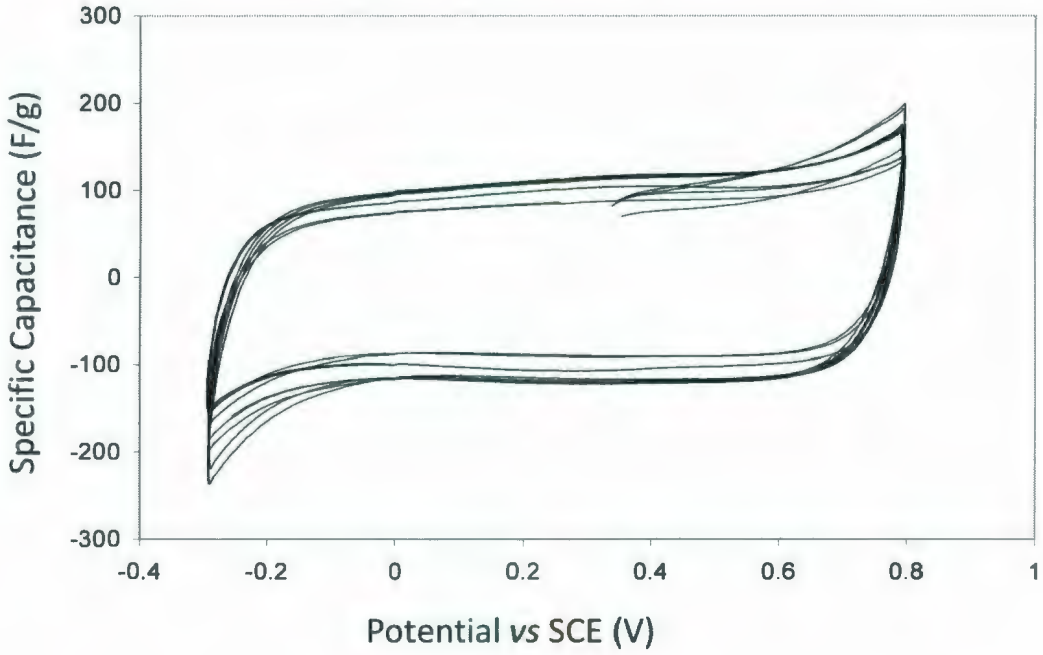
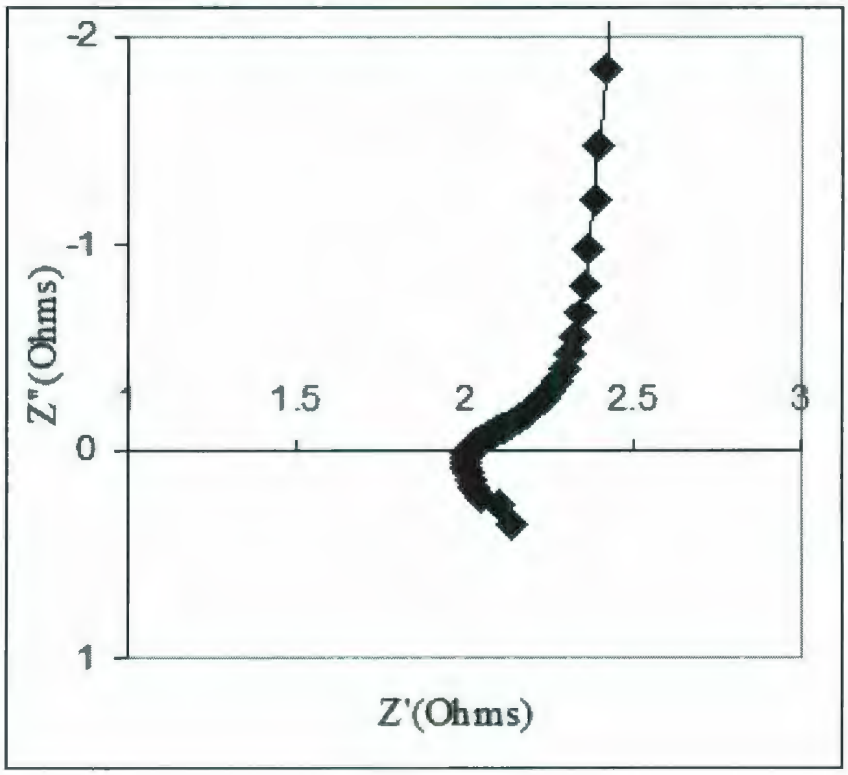


Figure 3.3B: An IS of an electrode containing BP + 5% Nafion



The Nafion concentration was changed to 10% and again CVs of 4 electrodes were taken. Table 3.3 displays these results. The CV on these electrodes revealed an average Cs of 107.8 +/- 15.8 F/g. These same 4 electrodes were tested by IS, and an average Cs of 80.3 +/- 15.2 F/g was obtained. A CV of one electrode is displayed in figure 3.4A. Similarly a representative IS is shown in figure 3.4B.

Table 3.3: Cs results for 4 BP electrodes containing 10% Nafion

Electrode #	Cs (F/g)
1	62.8
2	87.3
3	80.6
4	61.4

Figure 3.4 A: CV of a BP electrode containing 10% Nafion

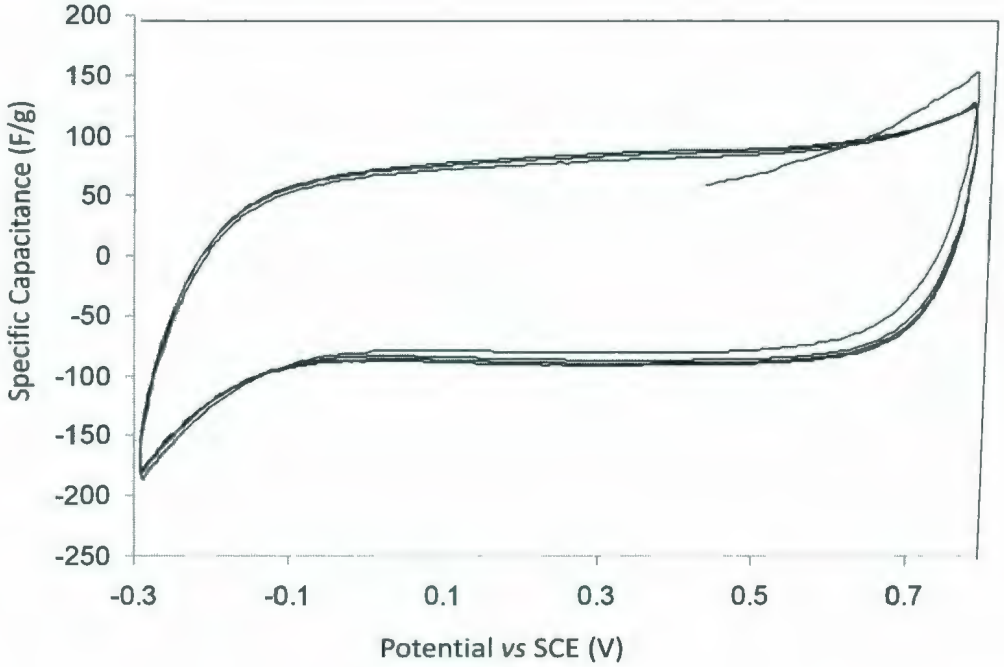
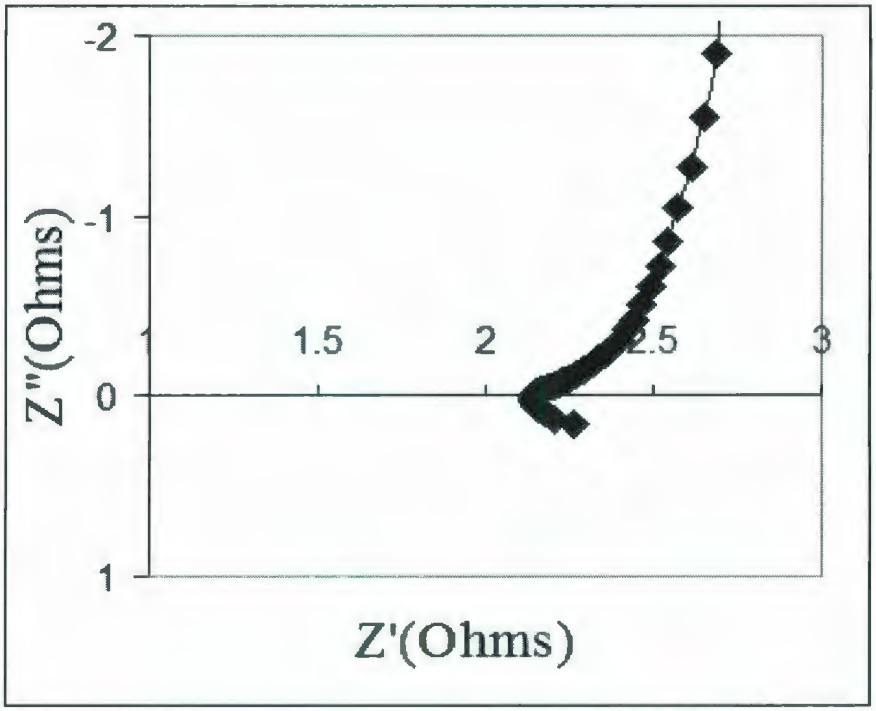


Figure 3.4B: IS of a BP electrode containing 10% Nafion



These results seemed to indicate that a lower concentration of Nafion was better, since it gave higher capacitances and lower resistances. Therefore, 0% was tested in much the same manner. From the CVs shown in Figure 3.5A and IS shown in Figure 3.5B, the peak Cs average was found to be 140 +/- 12.0 F/g from the CV and 117.3 +/- 13.1 F/g for impedance. Table 3.4 gives the individual results.

Table 3.4: Cs values from the CVs of electrodes containing no Nafion.

Electrode #	Cs (F/g)
1	142.5
2	152.0
3	125.5

Figure 3.5A: CVs of 3 BP electrodes containing no Nafion

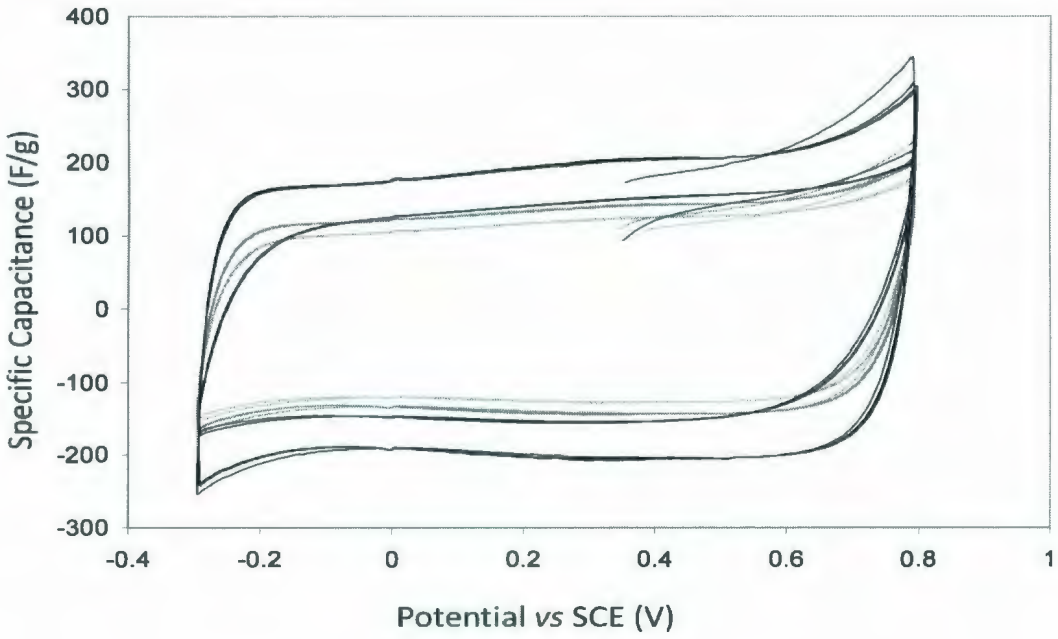
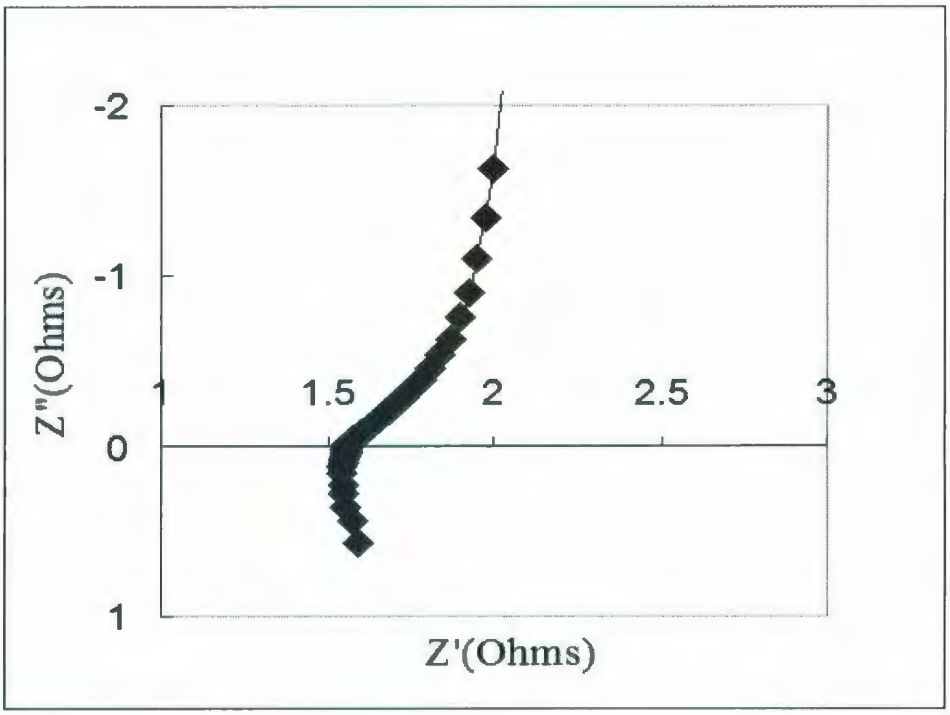


Figure 3.5B: IS of a representative BP electrode containing no Nafion.



As seen from the VCB at least **some** Nafion should be added to increase capacitance. 1% was tested with CV and the Cs results presented in table 3.5. CVs of these electrodes are displayed in figure 3.6A. A representative IS for 1% Nafion is shown in figure 3.6B.

Table 3.5: Cs results for 4 BP electrodes containing 1% Nafion

Electrode #	Cs (F/g)
1	125
2	139
3	128
4	156
5	126

Figure 3.6A: CVs of 5 BP electrodes containing 1 % Nafion

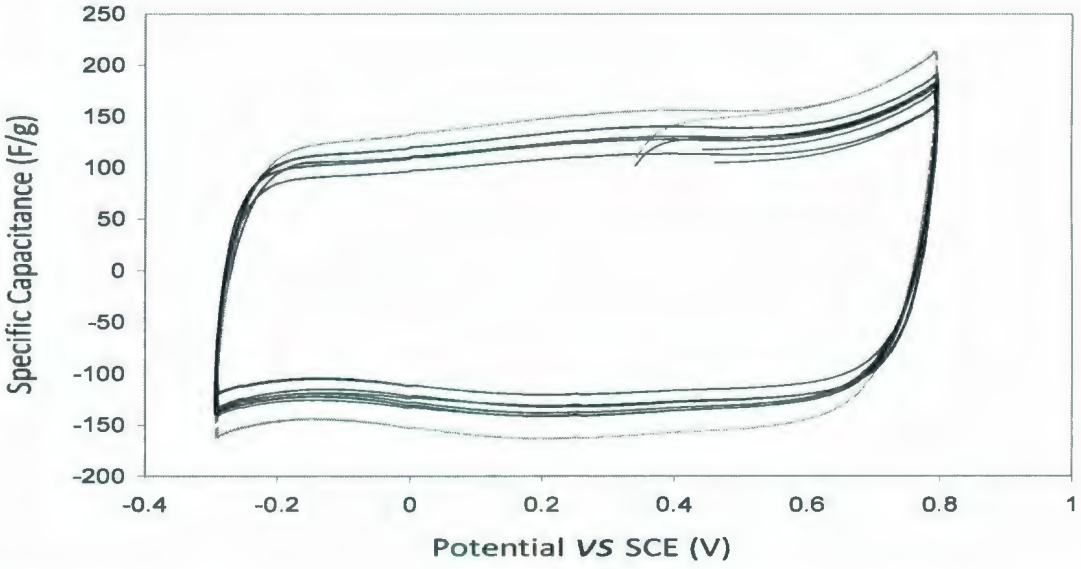
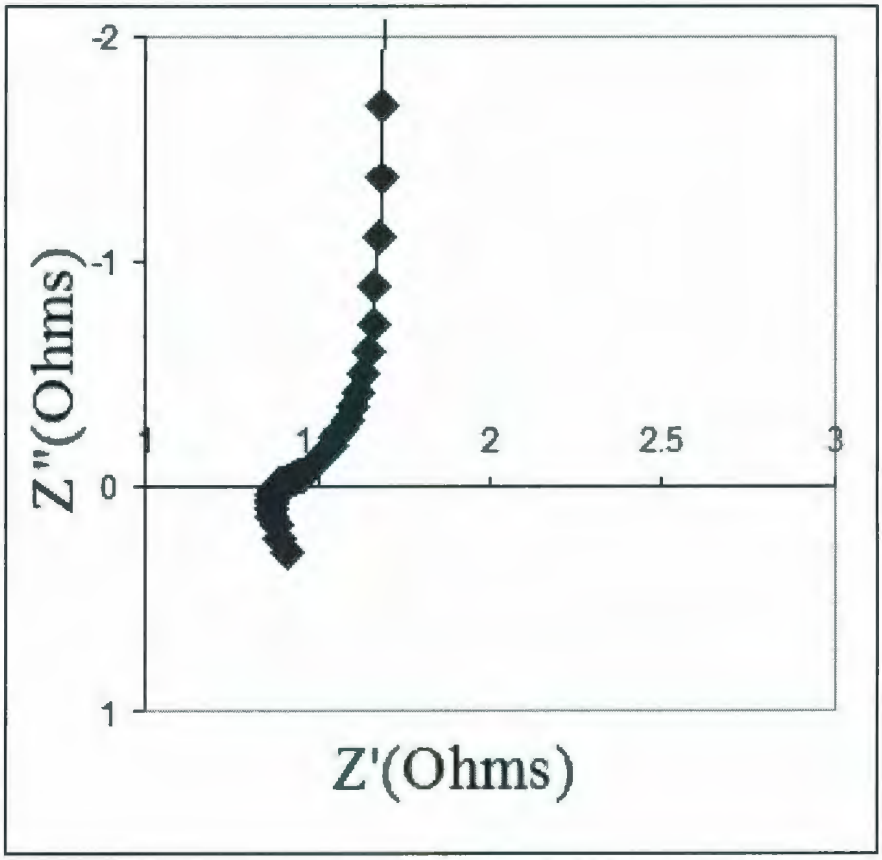
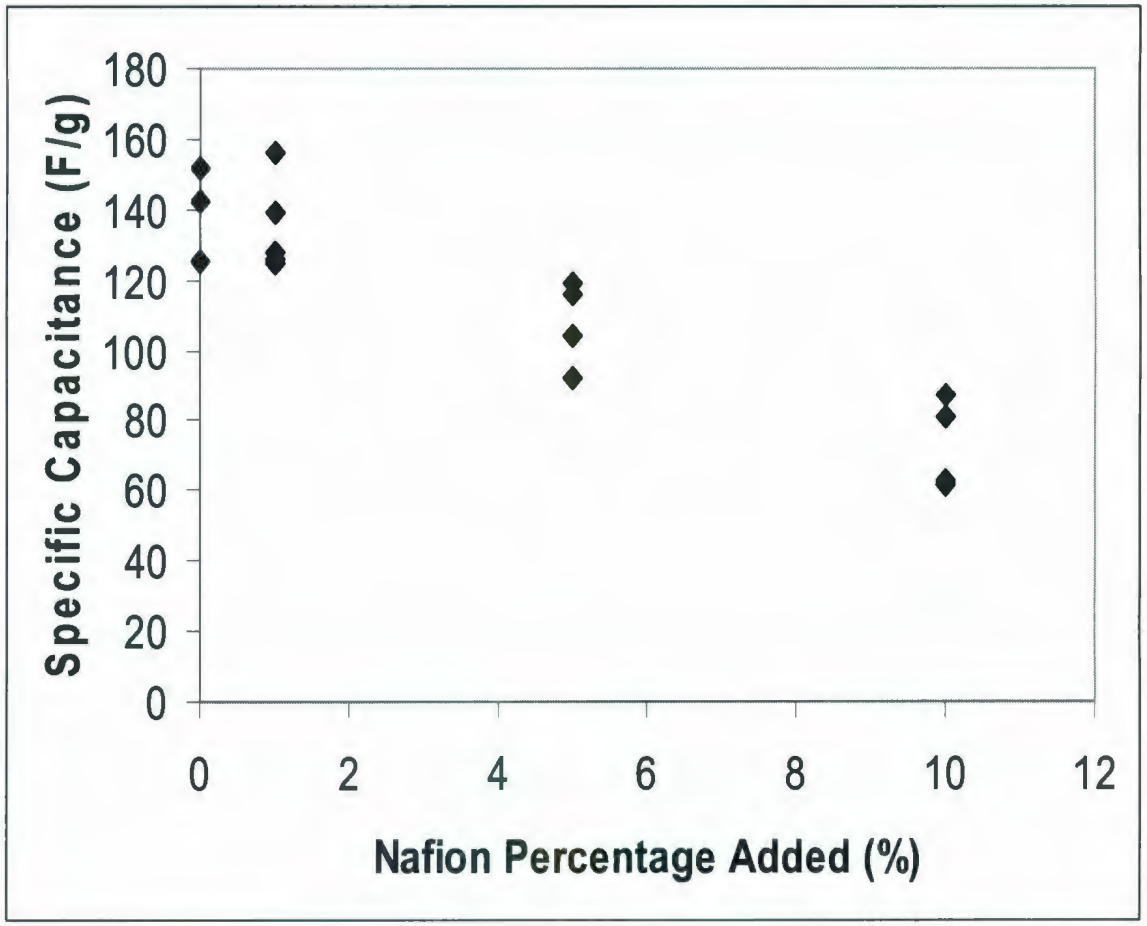


Figure 3.6B: An IS of a representative electrode with BP and 1% Nafion



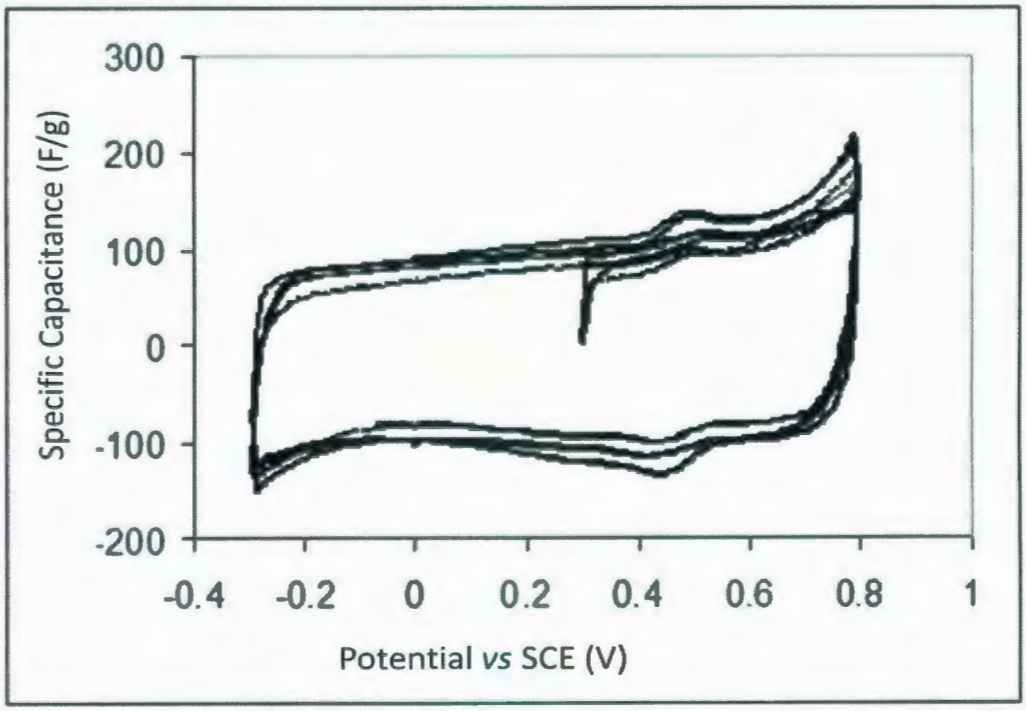
These experiments yielded average peak Cs values of 134.8 F/g +/- 21.2 F/g from the CV and 124.6 +/- 22.4 F/g from impedance. As can be seen by the extreme variability in the average Cs values, a clear optimum Nafion concentration was not found, but the Cs values in which 1% was used seemed to be the highest with the most consistency. Because of these findings 1% Nafion was used most frequently in future experiments. Figure 3.7 is a plot which presents Cs (F/g) versus Nafion concentration for each of the 4 concentrations used.

Figure 3.7: A plot of CV Cs results of BP electrodes containing various amounts of Nafion binder.



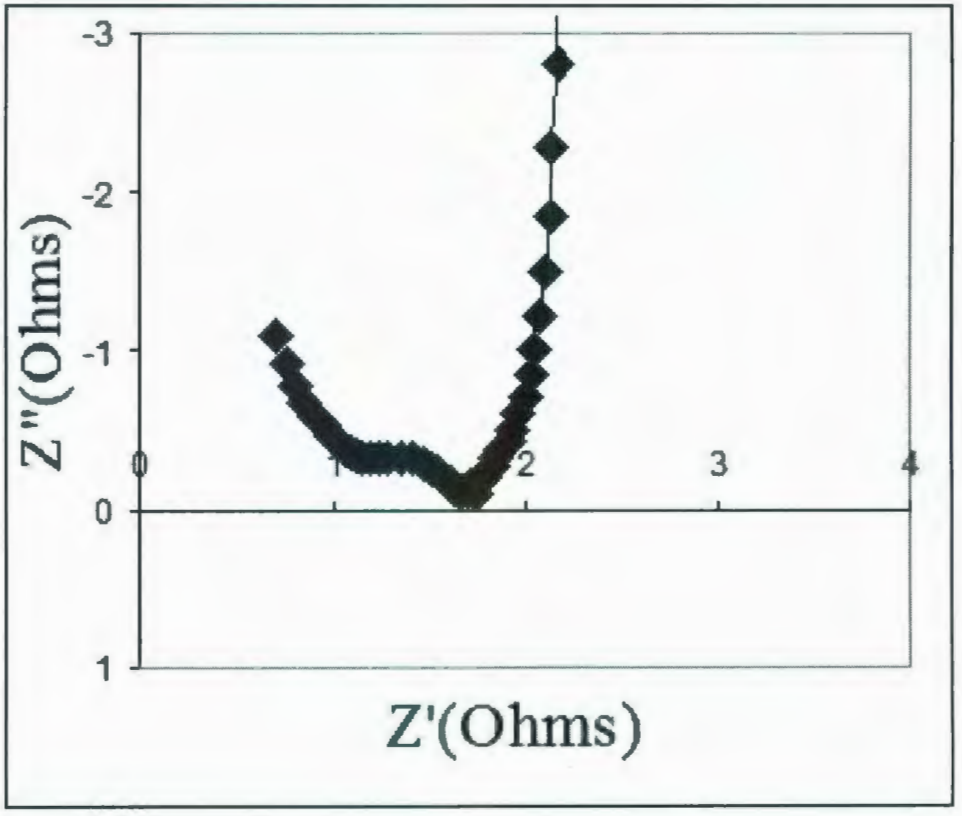
The 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane + tetramethylorthosilicate sol-gel described in Chapter 2 (2.1) was anticipated to be a good binder so it was tested with BP. The gel (i.e. SG taken out of the freezer for ~5hrs) was placed in a vial with the BP and isopropanol, and subsequently the resulting mixture was placed in an ultrasonic bath for approximately 5 min to ensure adequate assimilation. The original experiments employed a mixture containing 50% of both BP and SG. Using an average mass loading of 1.02 mg, four different sets of cyclic voltammagrams were taken of four different electrodes at 100 mV/s. The four CVs, which can be seen in figure 3.8, yielded an average peak Cs value of 108 +/- 17.2 F/g. This is a relatively low Cs value, especially considering black pearls and 1% Nafion yielded better results.

Figure 3.8: Four CVs of BP + 50%SG electrodes under a scan speed of 100 mV/s



The resistances of these four electrodes were tested by IS and one of the spectra can be seen in figure 3.9. Since the resistance was high, a sandwich cell (See chapter two, figure 2.4B) was constructed that greatly reduced the solution resistance (See chapter 2, 2.3.3).

Figure 3.9: An IS of a BP electrode containing 50% SG



3.3.2 Black Pearls in the Sandwich Cell

Sandwich cells (with various minor modifications (figs 2c d, e)) were used in the majority of experiments on BP. The Nafion content of the electrodes was varied in a small number of the experiments, but a value of 1% was usually used, leading to an average peak Cs value of 136 +/- 18.5 F/g. Figures 3.10A and B show CVs and IS spectra. The very low resistance values shown in the figure indicate that the solution resistance was greatly reduced by use of the sandwich configuration.

Figure 3.10A: CVs of two BP + 1% Nafion electrodes that were tested in the sandwich cell.

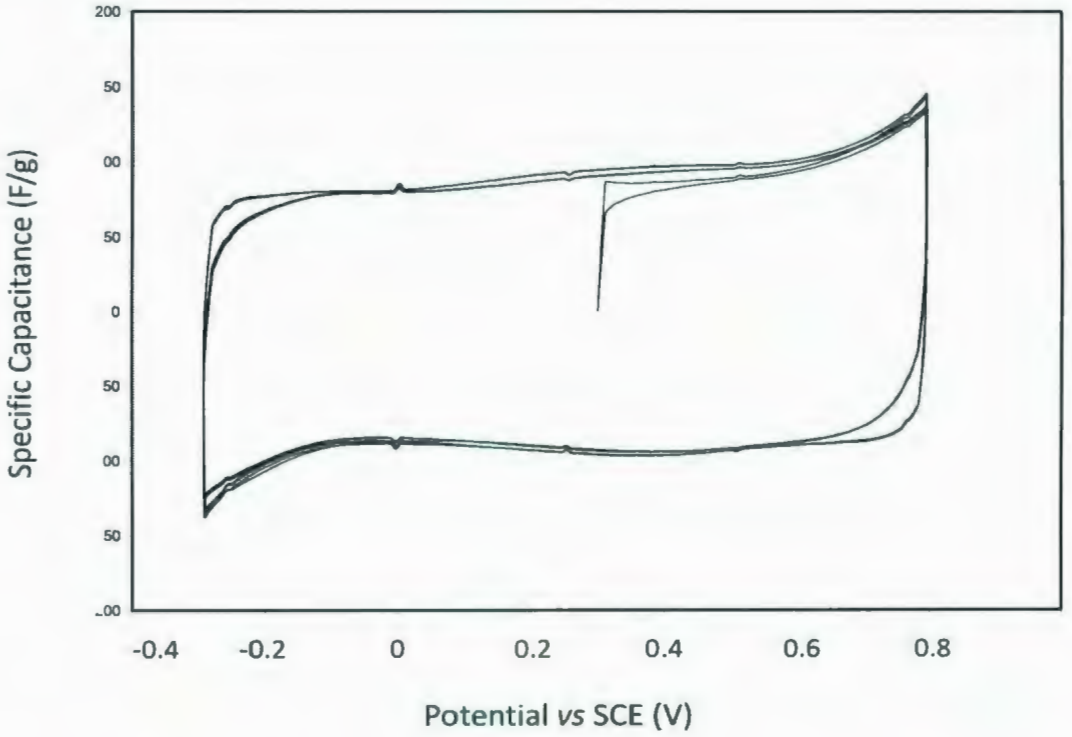
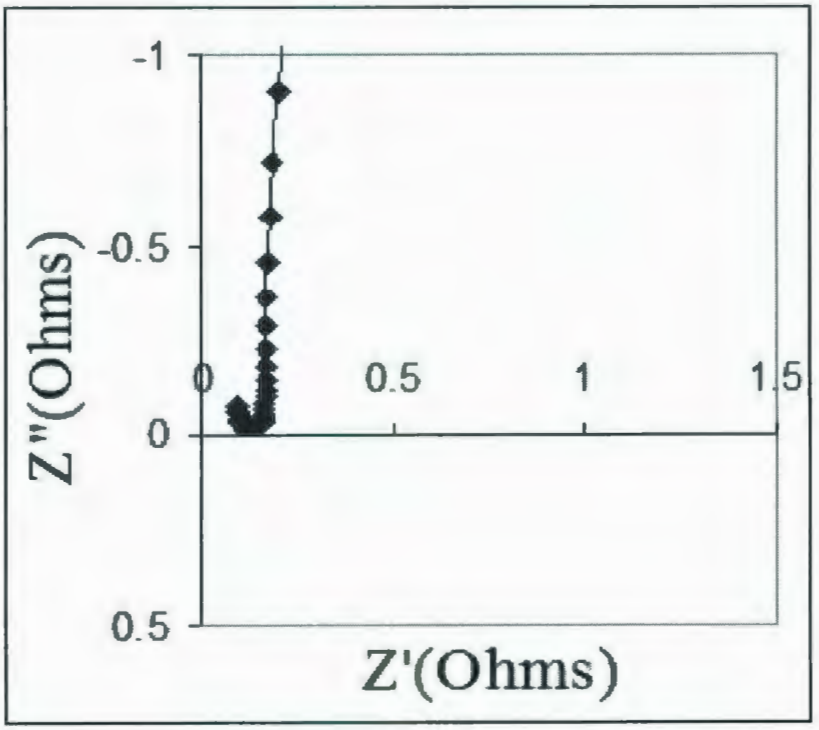


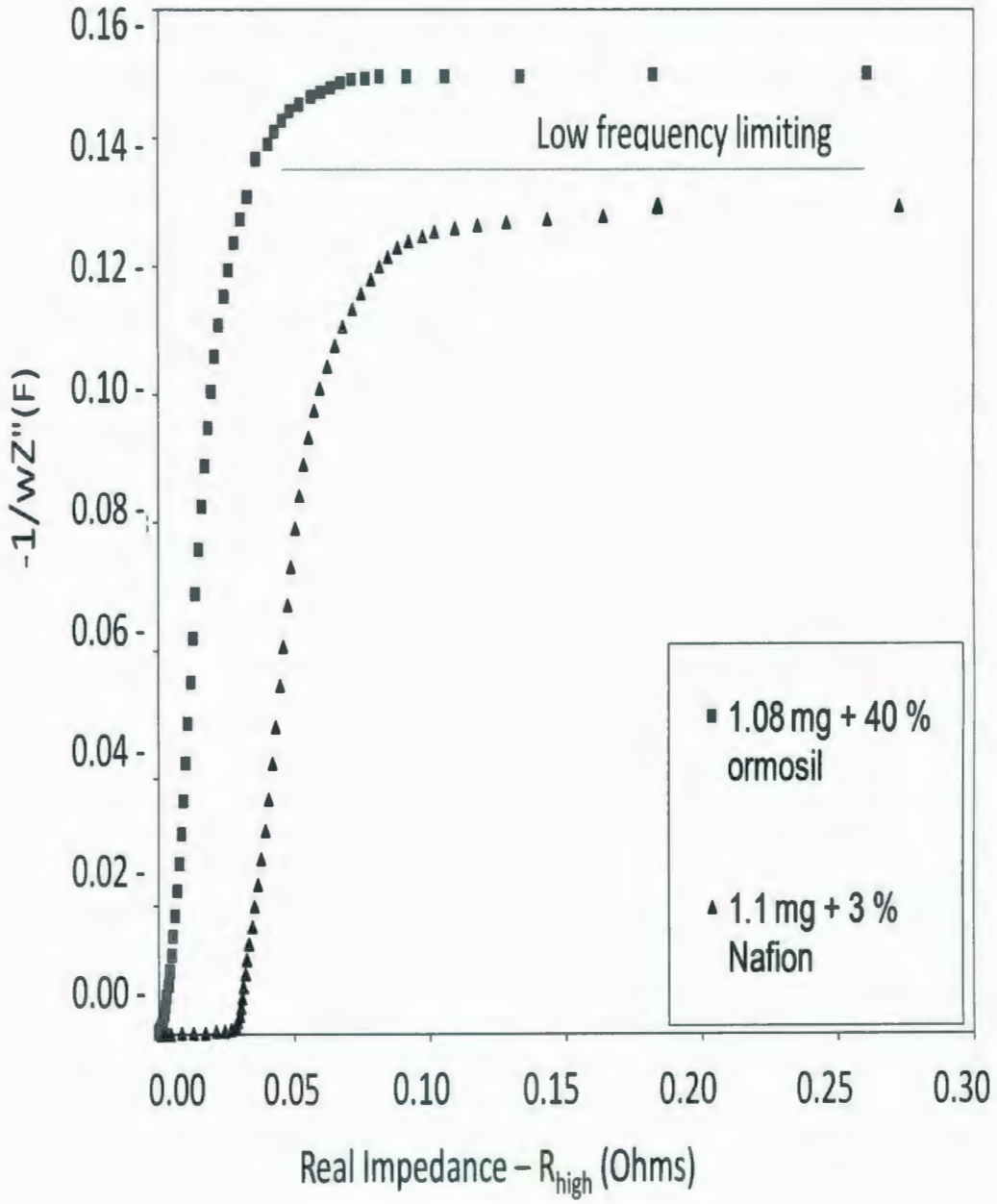
Figure 3.10B: IS of a BP + 1%Nafion electrode that was tested in the sandwich cell.



3.3.3. Comparison of Nafion and Sol-Gel Binders

The use of Nafion as a binder has been shown to provide an effective proton path for charge transfer. As the name implies it binds the carbon particles together so, ideally, they act as a single larger porous particle.[7] The Nafion and SG results can best be compared as plots of the capacitance versus the resistance as shown in figure 3.11. This plot show several features. Firstly it is seen that more SG seems to lead to higher capacitance at lower resistance as can be seen in a comparison of the result with 40% ormasil (SG) and the results of the electrode containing a much smaller concentration of Nafion , but as shown by the figure, the 40% SG only leads to a 0.02 increase in the capacitance versus the resistance over the more efficient electrode using the about 10 times less binder. So while the extreme amount of SG increases capacitance it does not increase the capacitance enough to justify this increase in mass, since it lowers the specific capacitance.

Figure 3.11: Plots of the capacitance versus the resistance comparing BP + Nafion electrodes with BP + SG electrodes



3.3.4. Loading

Cs was found to depend on the mass loading in these studies. As can be seen in figure 3.12, which shows specific capacitance versus mass loading, very high Cs values were achieved at very low mass loadings using 1% Nafion binder (a similar trend was seen when SG was used). While this drops steeply in the beginning, very small differences in Cs values occur after the loading has surpassed 5 mg. This has been reported quite frequently in the literature, but at this time a plausible explanation has not been provided.

Figure 3.12 Specific capacitances of BP electrodes versus the mass of BP when 1% Nafion was used as a binder

3.3.5 Morphology of Black Pearls on CFP Electrodes

Two SEM images of a BP electrode were taken at increasing magnifications and are shown in figures 3.13A and 3.13B. These images clearly indicate that the powder (the flat areas) had infiltrated the CFP (the rods). Since the flat areas look quite homogenous the Nafion clearly binds the particles together effectively.

Figure 3.13A: An SEM image of a BP +1% Nafion electrode magnified 270X

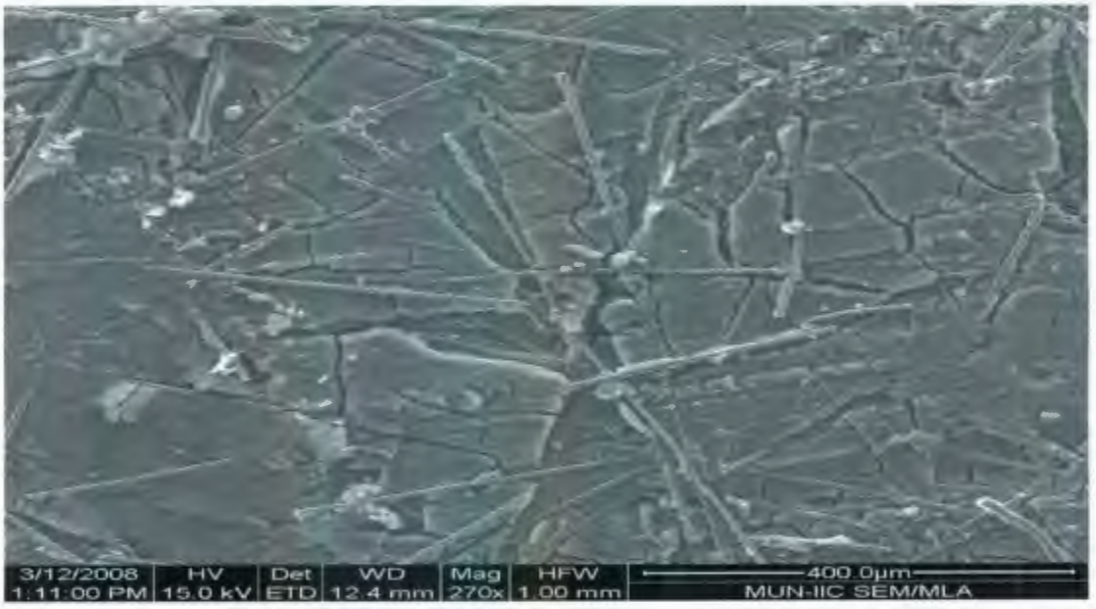


Figure 3.13B: An SEM image of a BP +1% Nafion electrode magnified 1352X

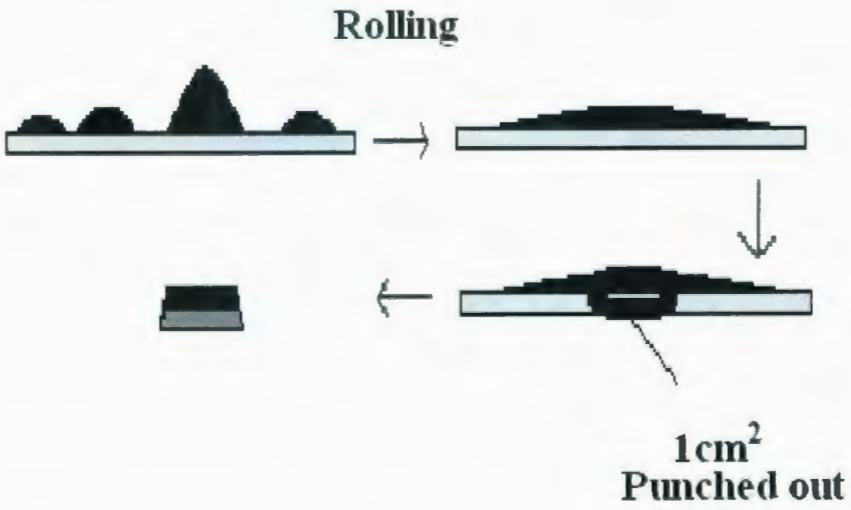
3.4 HIGH LOADING BLACK PEARLS ELECTRODES

The main purpose of the work described in this section was to increase the mass loading while maintaining a useful Cs. One important parameter that was taken into account was the capacitance (i.e. Cs x mass) in Farads. This is very important in applications of supercapacitors, because a large amount of energy generally needs to be transferred. Since a low resistance is also required for high power transfer, electrodes were tested in the sandwich cell.

The procedure used here may seem counterintuitive as it uses Teflon as one of the components. Because Teflon is hydrophobic it should have an adverse interaction with the aqueous electrolyte used (H_2SO_4), but it was found that when Teflon was used as a binder the electrodes showed good performance and stability.

Electrodes were prepared according roughly to Toupin et al.[6] as follows: 5% VCB, 90% BP and 5% Teflon were mixed in a vial with a small amount of methanol. The vial was then placed in an ultrasonic bath for ~5 min to ensure adequate mixing of the components. This procedure was slightly modified in this work with the 5% VCB being replaced by 5% Nafion. This recipe was tinkered with extensively including the complete removal of the Teflon (i.e. 10% Nafion) and the use of SG in lieu of the Nafion (i.e. 5% SG and 5% Teflon). None of the variations to the original recipe affect the Cs results significantly, so as using 5% Teflon, 5% Nafion, and 90% BP proved to be the easiest (i.e. best stability) it was used the most frequently. The procedure for using this method to create electrodes is outlined in figure 3.14.[6]

Figure 3.14: This figure depicts the typical assembly of an electrode possessing a high mass loading. The mixture described in the text is poured out of the vial onto a thin sheet of Teflon (solid as opposed to liquid suspension used in the mixture) forming numerous small clumps. These clumps are then combined by rolling them out into a thin sheet; a circle is cut out of the sheet using a $1cm^2$ hole punch.



3.4.1 Capacitance and Resistance

Three electrodes massing between 7.6 mg and 21.1 mg were tested by CV, with a low scan speed of 5 mV/s, and IS with a frequency range of 65 000 – 0.01 Hz. The electrodes' CVs and a representative IS are displayed in figures 3.15A and B, respectively. Table 3.6 displays Cs results for these three electrodes.

Figure 3.15A: The CVs of 3 preliminary (5% Teflon, 5%Nafion and 90% BP) carbon dough electrodes

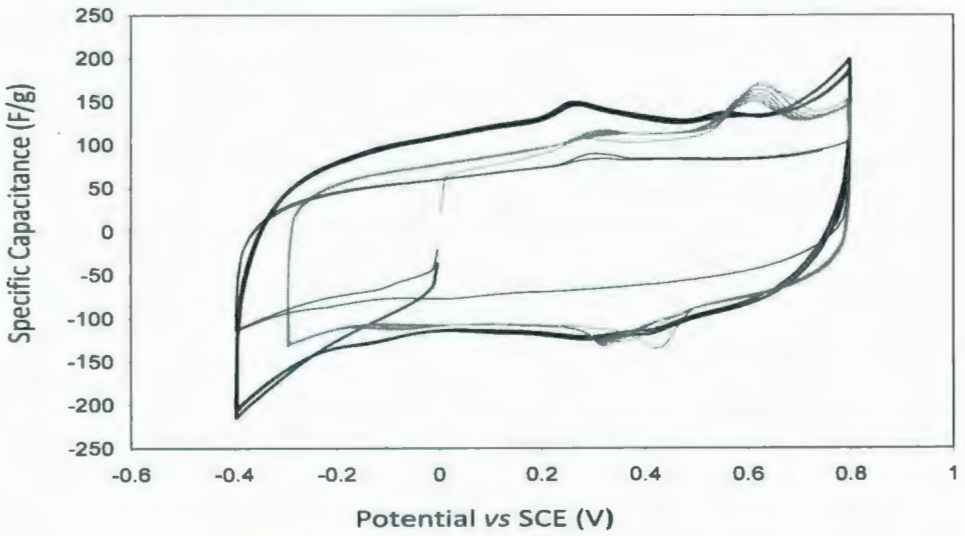


Figure 3.15B: The IS of a preliminary (5% Teflon, 5%Nafion and 90% BP) carbon dough electrode

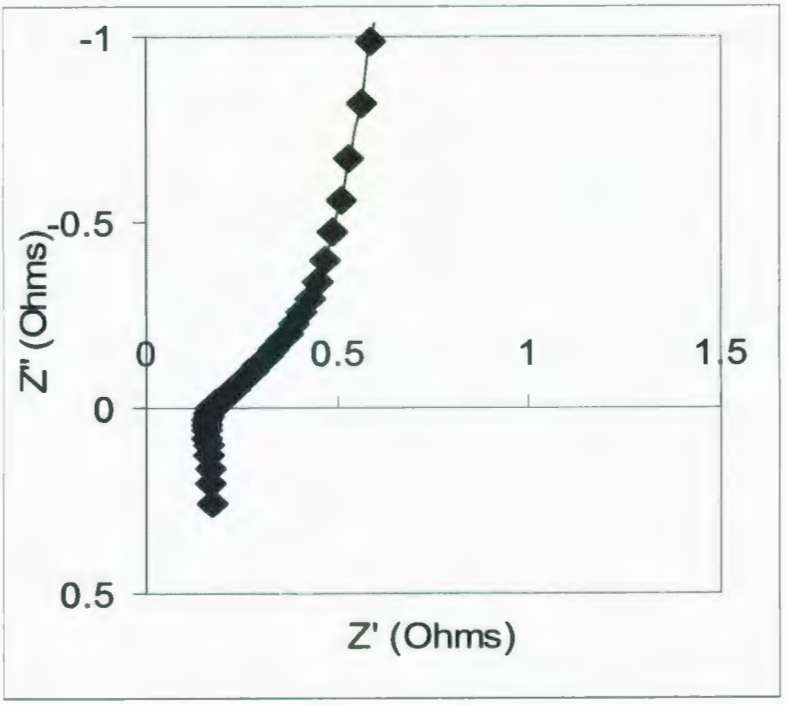


Table 3.6: Peak Cs values obtained by CV on three preliminary carbon dough electrodes (see pg 56)

Electrode #	Cs (F/g)	Mass (mg)
1	147	14.0
2	117	31.1
3	70.3	21

The average peak Cs from the CVs (which are shown in figure 3.15A) was 111.4 +/- 41.1 F/g and a relatively high average capacitance (Cs x mass) of 1.14 F +/- 0.34 F was found. And while it can clearly be seen from figure 3.16B that the resistance is somewhat high (~0.4Ω), it is reasonable considering the high mass loading.

In the original paper where this method was developed, (see reference 6) 5% VCB was used, but no explanation was given as to why. Because of this 5%VCB was added to the recipe, and a mixture was made up. Two electrodes were made, and CVs and an IS were taken. These are displayed in figures 3.16A and B, respectively. The addition of the VCB did not lead to a higher Cs value.

Figure 3.16A: CVs of two dough electrodes containing 5% VCB with loadings of 14.0 and 21.1 mg

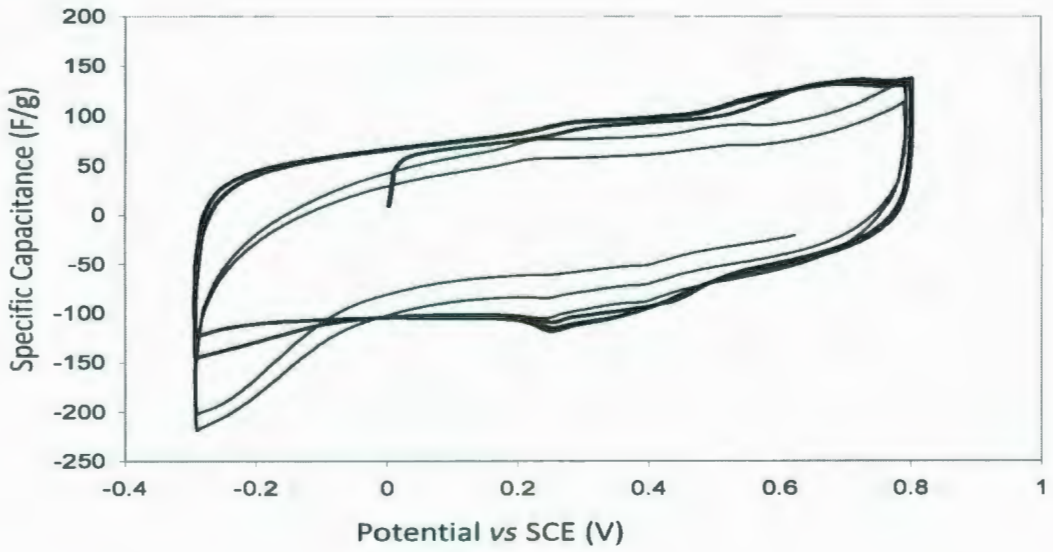
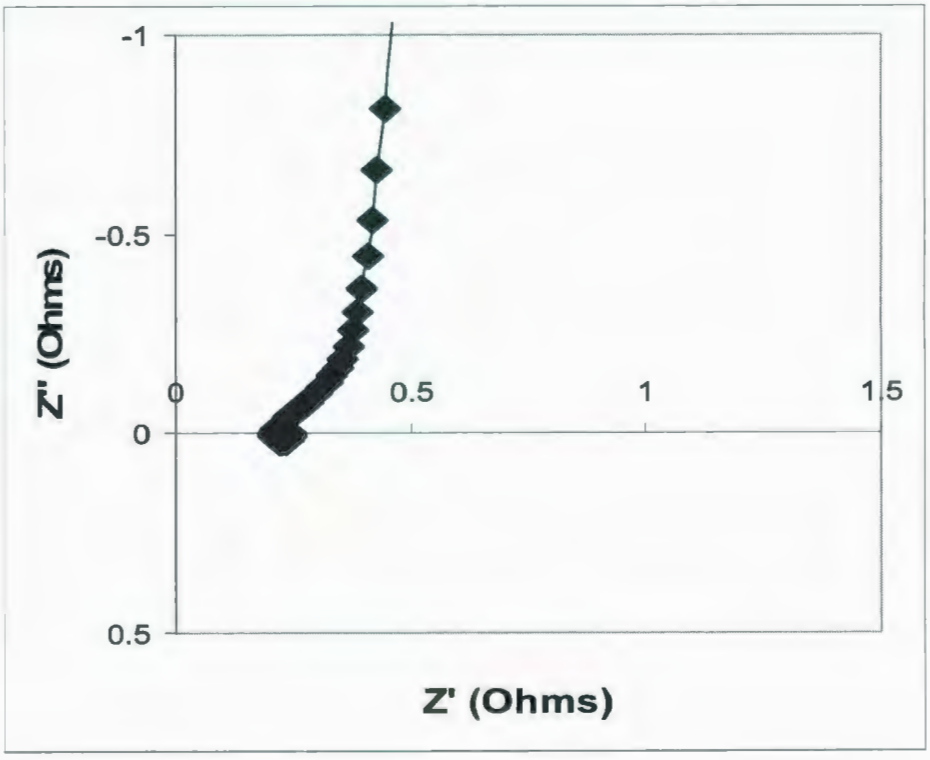
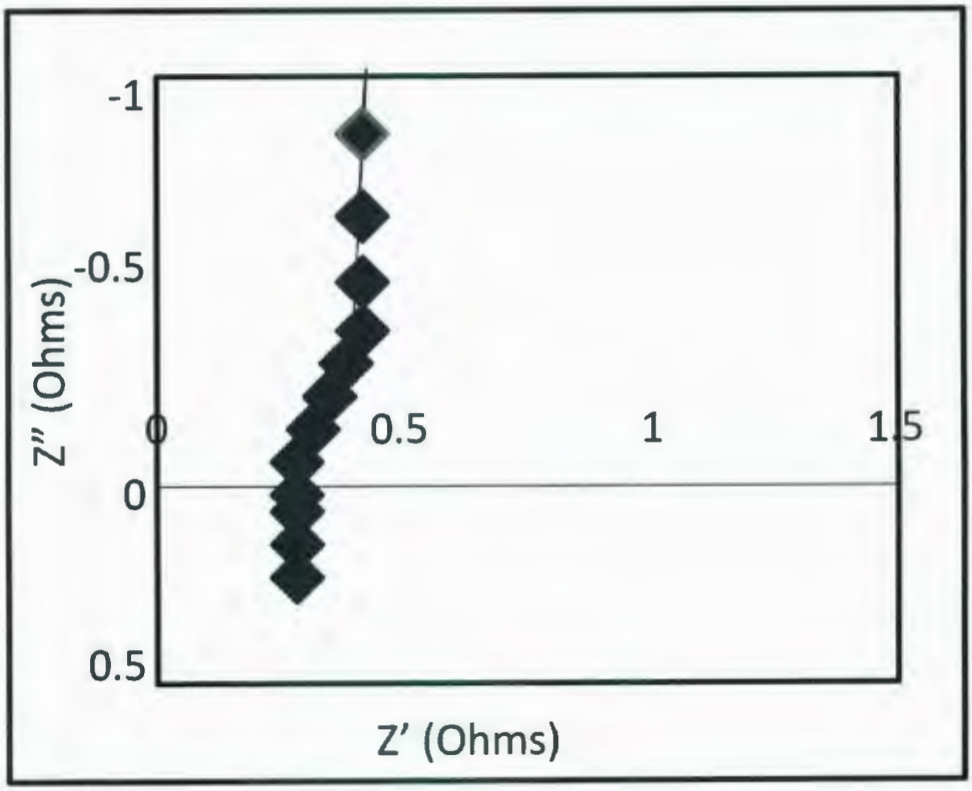


Figure 3.16B: An IS spectrum of a dough electrode containing 5% VCB with a loading 14.0 mg



It was thought that the resistances associated with these electrodes could be decreased by adding a quantity of SG, and so ~10% SG was added to 90% (BP + Teflon). An IS was taken (figure 3.18) leading to a resistance value of approximately 0.3 Ω.

Figure 3.17: An IS taken of a carbon dough electrode containing SG with a loading of 13.2 mg



While the SG addition did lower the resistance value, the Cs remained somewhat low. Because Nafion was shown to be able to significantly raise capacitance values in past experiments it was tested in these electrodes. In order to test the validity of using Nafion to make thicker films, a mixture containing 88% BP, 6% Teflon and 6% Nafion was prepared, combined with MeOH, sonicated, placed in the sandwich cell, and tested using CV and IS. The spectra are shown in 3.18A, and 3.18B.

Figure 3.18A: A CV of dough electrode containing Nafion binder (6%) with a mass loading of 14.6 mg.

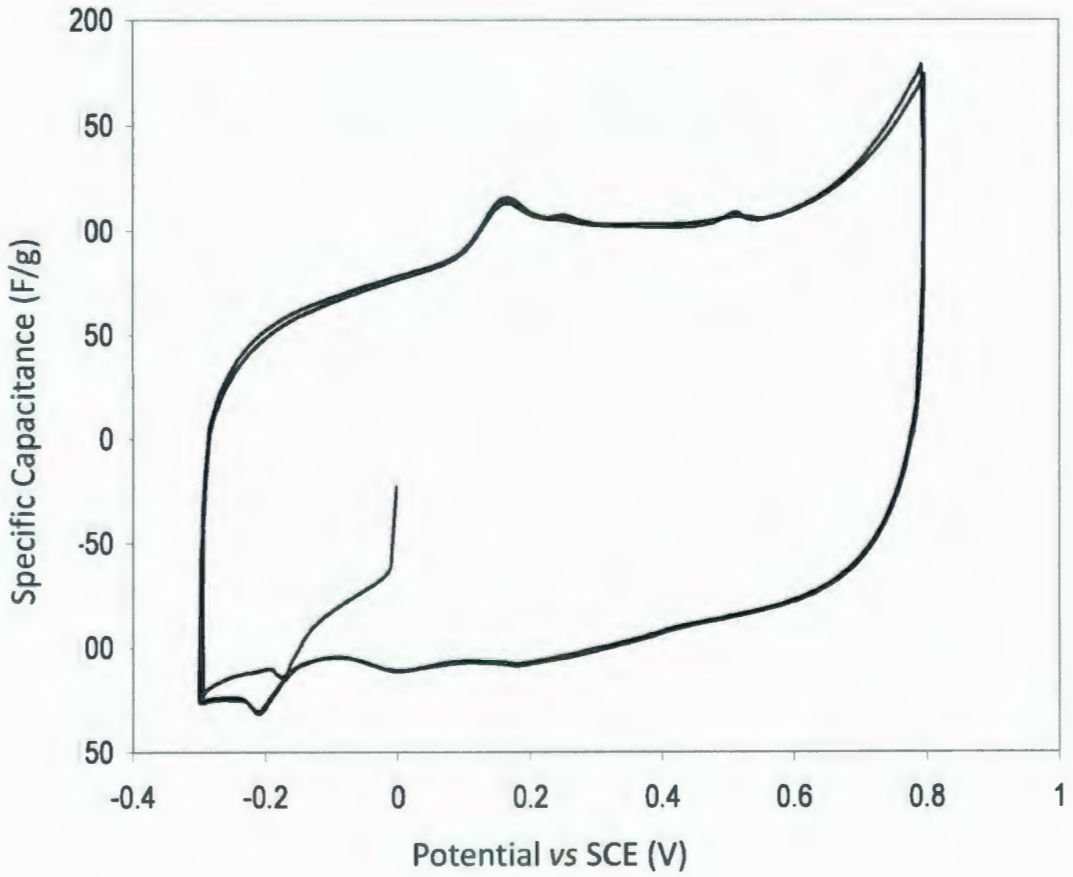
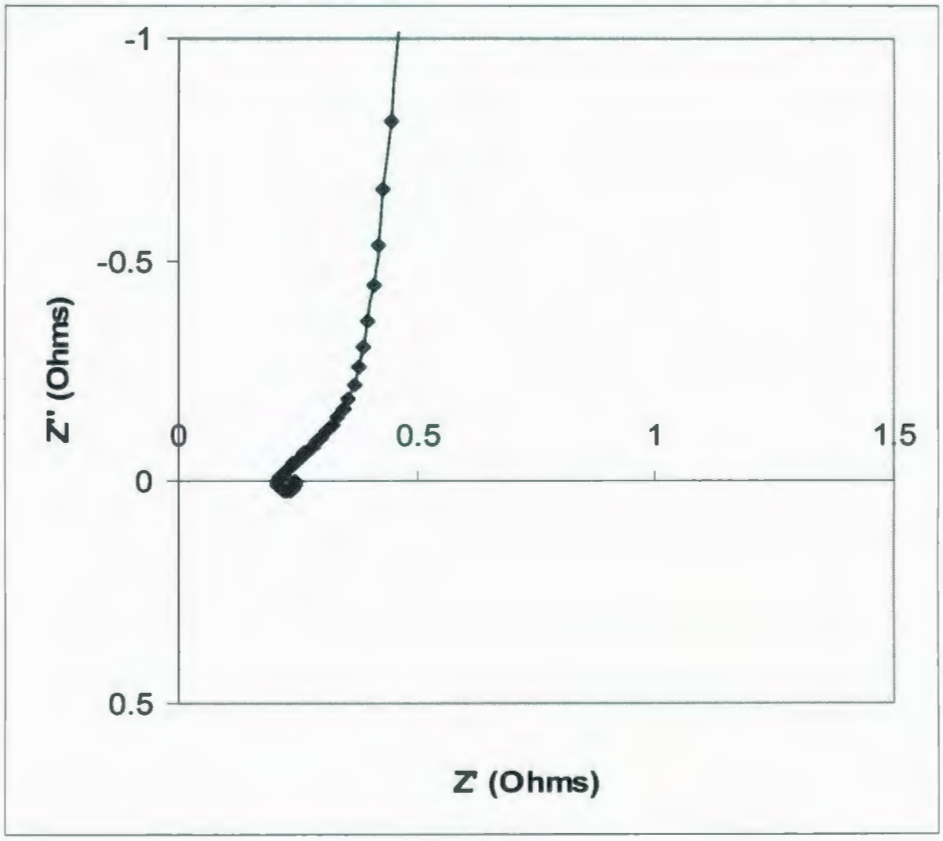


Figure 3.18B: An IS of dough electrode containing Nafion binder (6%) with a mass loading of 14.6 mg.



As can be seen, this electrode had an extremely low resistance, and so at least some Nafion was used in all future experiments. Seeing as how the results from this experiment were so good, an electrode was constructed using only Nafion (10%) and BP. As soaking in H_2SO_4 seemed to increase the Nafion's affect on the capacitance, this electrode was left in a vial of electrolyte for 22 h prior to the experiment. A CV and IS of this 8.0 mg electrode were taken and are shown in figure 3.19A and 3.19B. The Cs was

found to be 132.5 F/g, and the resistance was found to be 0.5 Ω. It appeared that Nafion alone, increased the capacitance but also increased the resistance by over 0.1 Ω; because of this Nafion in combination with Teflon was used in most future experiments.

Figure 3.19A: A CV of a dough electrode containing Nafion (10%) as the binder.

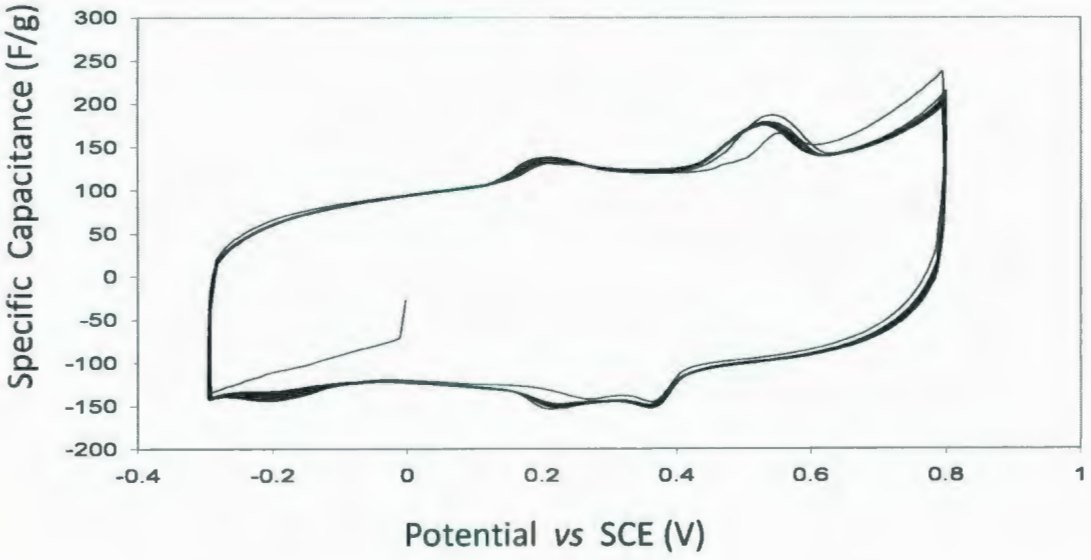
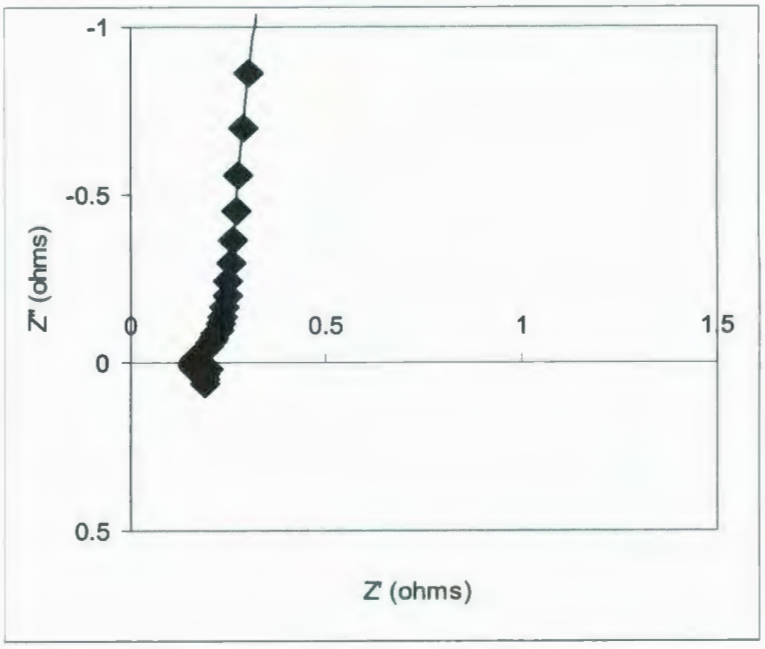


Figure 3.19B: An IS of a dough electrode containing Nafion (10%) as the binder.



Teflon and Nafion were used (5% each) in two electrodes that were subjected to a new H_2SO_4 infiltration method; 1-2 drops of 1 M H_2SO_4 were added to each electrode using a disposable glass pipette. These two electrodes were then placed in a Petri dish for 16 hrs to allow the acid adequate time to soak in. After the electrodes were taken out of the dish, they were each placed in a separate sandwich cell and had CV and IS run on them which are shown in figures 3.20A and 3.20B. The CV gave an average peak Cs of 148.8 F/g and impedance spectra on these two electrodes gave an average resistance value of 0.25Ω. Table 3.7 shows these characteristics for each electrode.

Table 3.7: Characteristics of 2 dough electrodes (containing 5% Nafion and 5% Teflon)

Electrode	Cs (F/g)	Resistance (Ω)	Mass (mg)
1	149.6	0.23	14.9
2	148.0	0.27	16.3

Figure 3.20A: CVs of two 1 M H_2SO_4 treated dough electrodes (containing 5% Nafion and 5% Teflon).

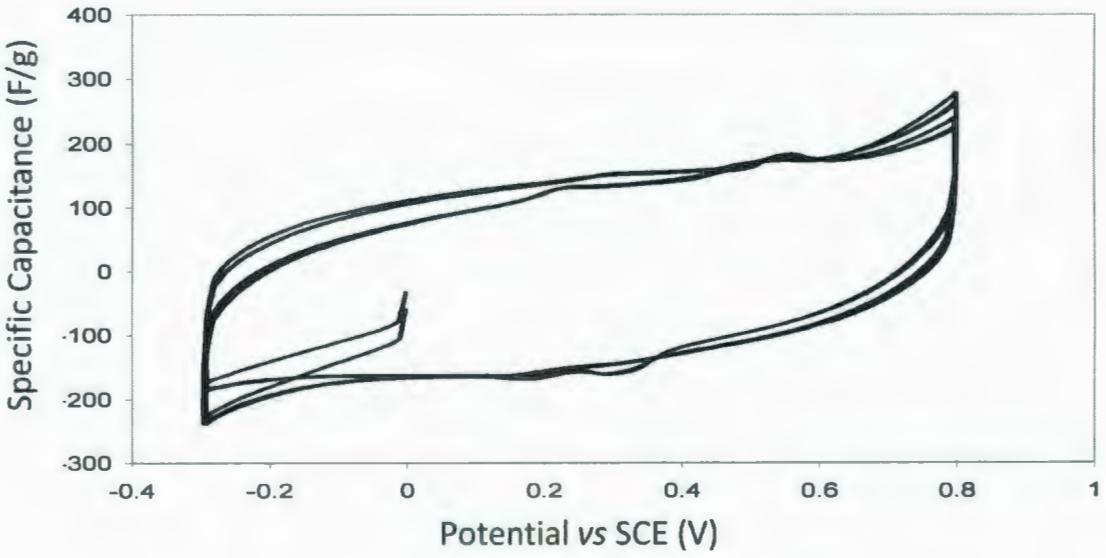
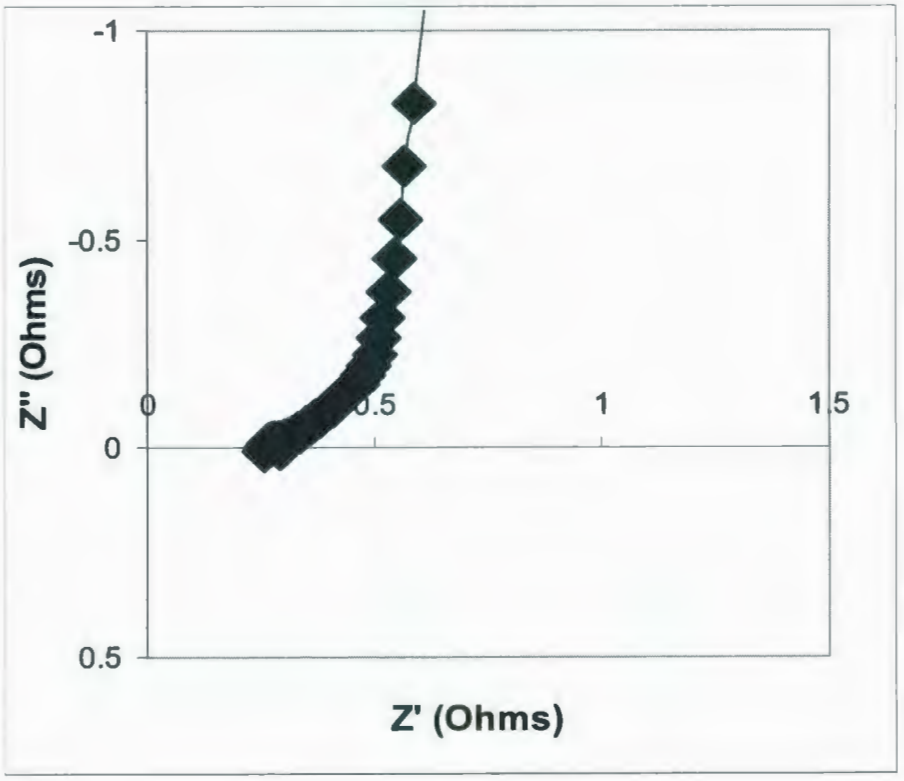
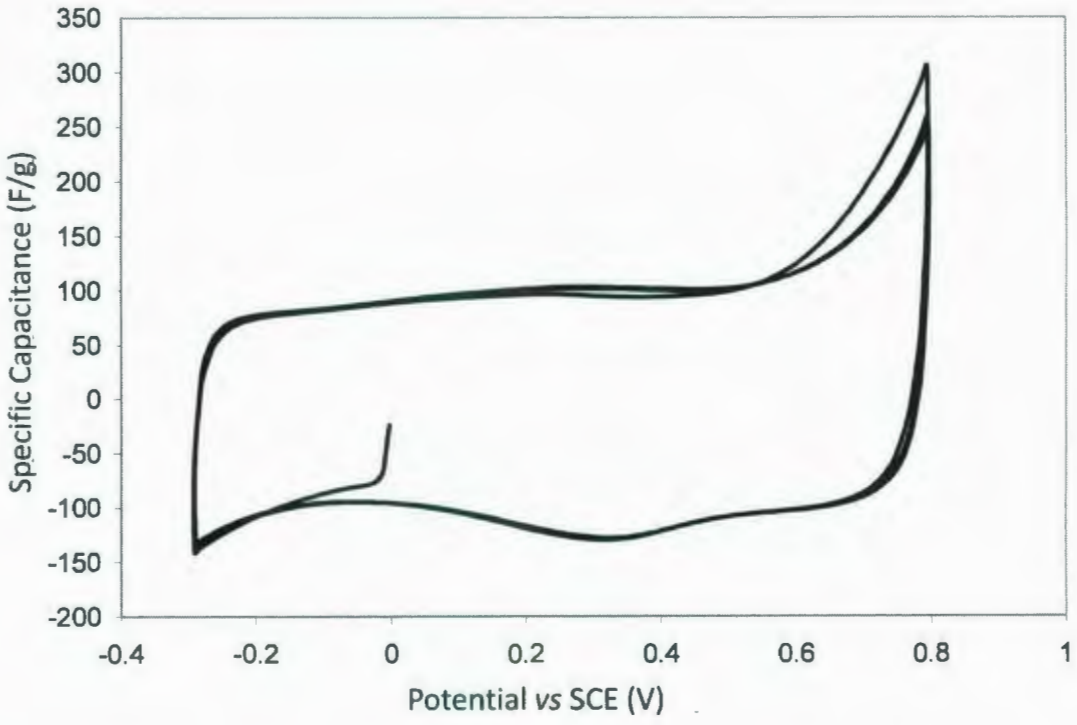


Figure 3.20B: An IS of a 1 M H_2SO_4 treated dough electrode (containing 5% Nafion and 5% Teflon)



Another electrode was prepared in much the same matter with one big difference; the BP, Teflon and Nafion were mixed with a larger volume (~2ml) of methanol. It was theorized that the Teflon and Nafion may not uniformly disperse in BP mixtures containing a small amount of MeOH. This mixture was then placed in an ultrasonic bath for ~10 min, then heated (slightly) to remove the excess methanol and finally rolled out as usual and fashioned into a disk electrode. When this process was completed a much higher mass loading of 30.7 mg was achieved. A CV, which can be seen in figure 3.21, yielded a Cs of 117 F/g (not the highest) but a very impressive capacitance value of 3.59 F.

Figure 3.21: A CV of a 30.7 mg BP electrode



The capacitance is only impressive if a reasonable resistance value accompanies it, and an excellent resistance value of 0.13 Ω was found from IS. The higher capacitance may be due to the fact that the mass was more evenly distributed on top of the CFP due to the fact that for this experiment a slightly larger piece (1.4 cm^2) of CFP was used.

Three more tests similar to the previous one were performed, again by CV (see figure 3.22A) and IS (see figure 3.22B); the Cs results obtained by CV are displayed in table 3.7. An average Cs of 112.5 +/- 21.5 F/g was found.

Figure 3.22A: CV results for 3 very high loading BP electrodes

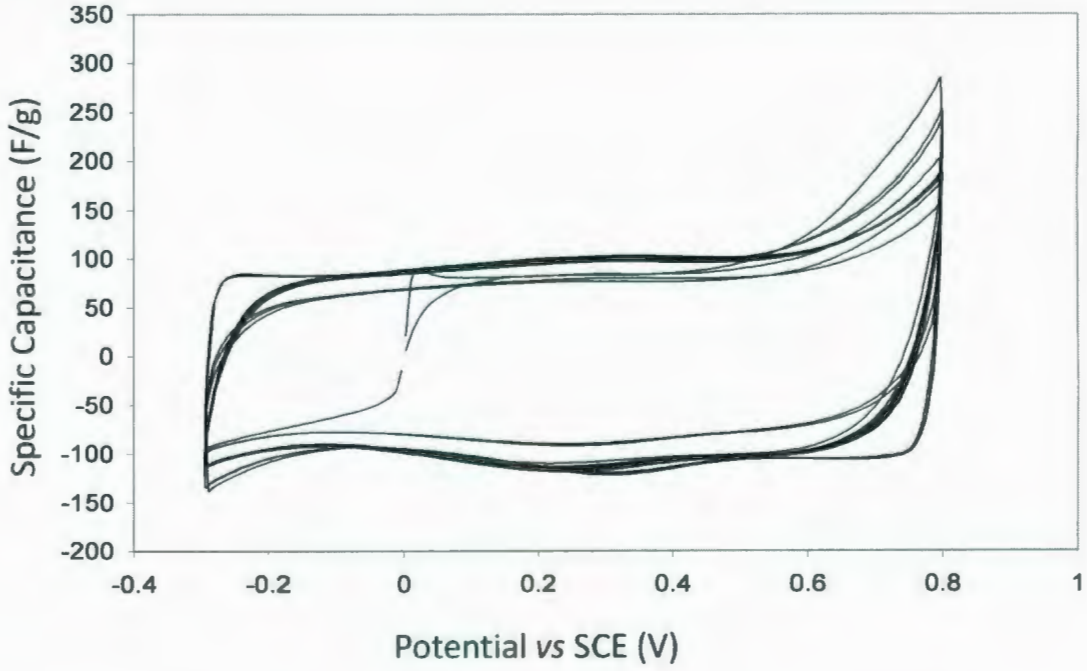
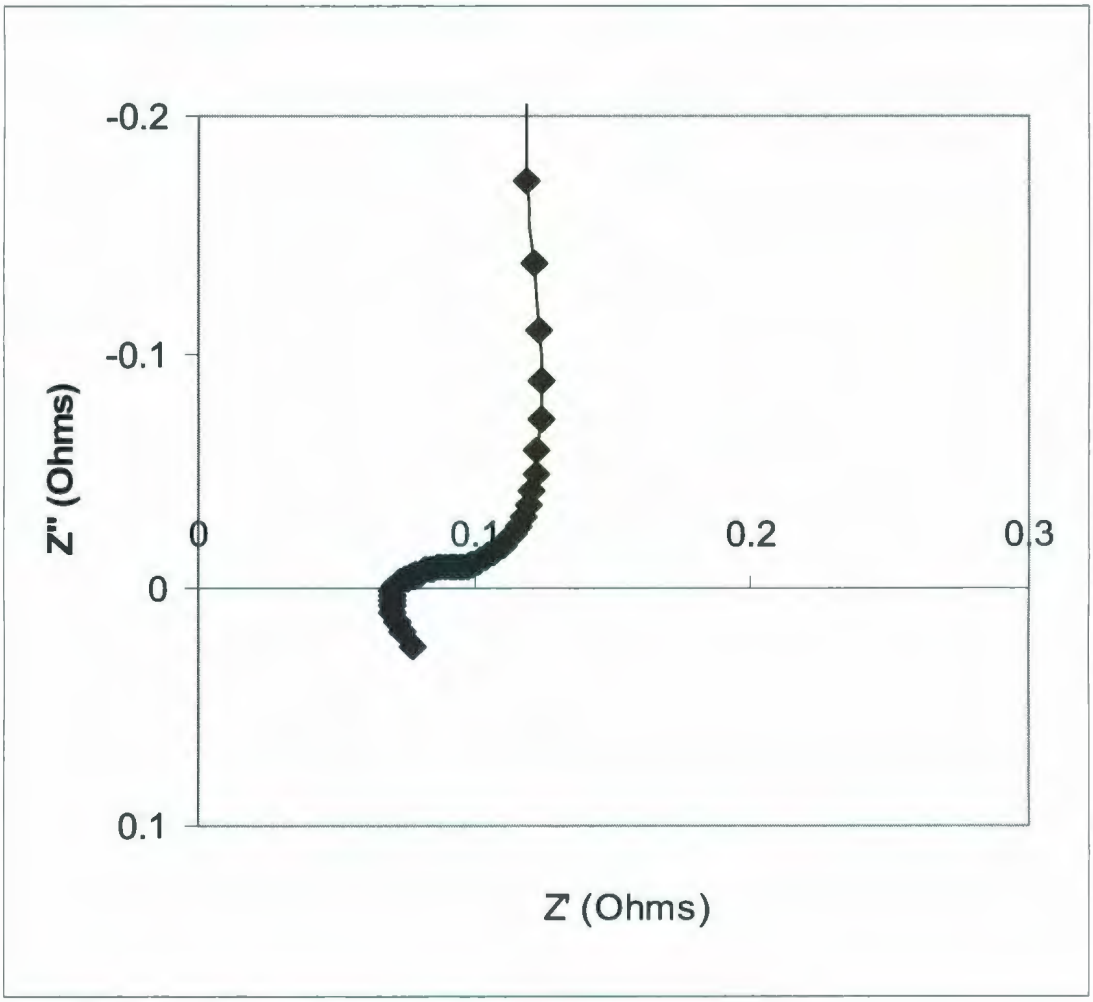


Figure 3.22B: IS result for a very high loading (24.4 mg) BP electrode using the standard Teflon/Nafion amounts



These results were very promising, so it was proposed that the SG may help make even higher loadings. An electrode massing 11.5 mg was made from a mixture of 2/3 BP and 1/3 SG, and was tested by CV and IS. The CV revealed a Cs of 107 F/g (C = 1.23 F) and the IS revealed a very low resistance of ~0.18 Ω. The electrode was then allowed to

soak in the electrolyte for 16 hrs. A new CV and IS were taken (figures 3.23 A & B) giving a very high Cs of 321 F/g and also a higher (but not drastically) resistance.

Figure 3.23A: A CV of a SG dough electrode before (-----) and after (▬) soaking

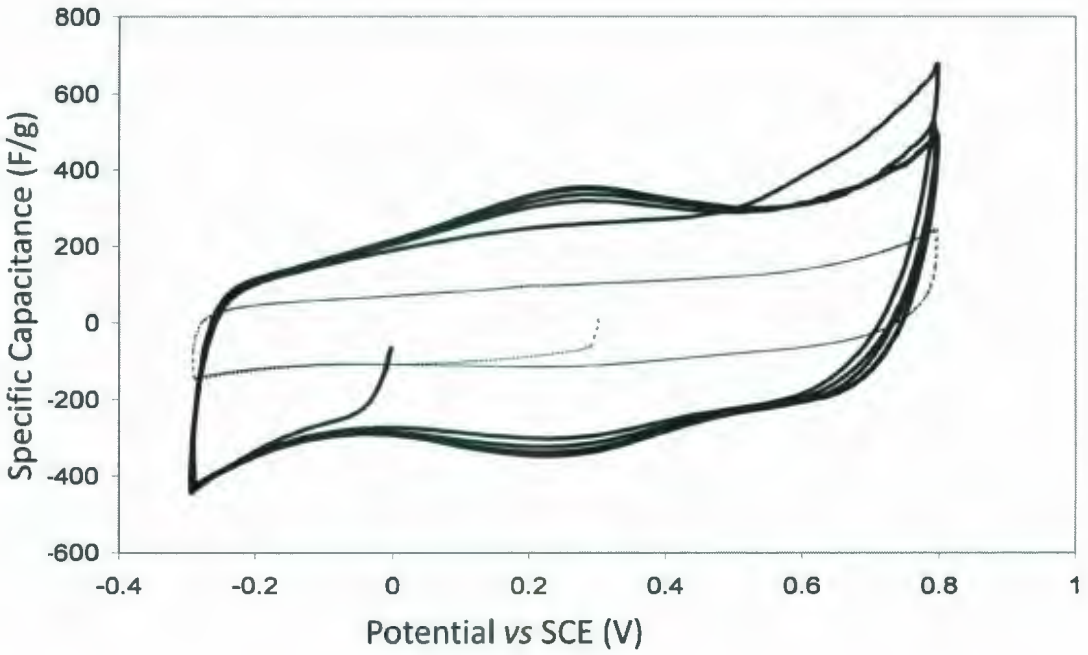
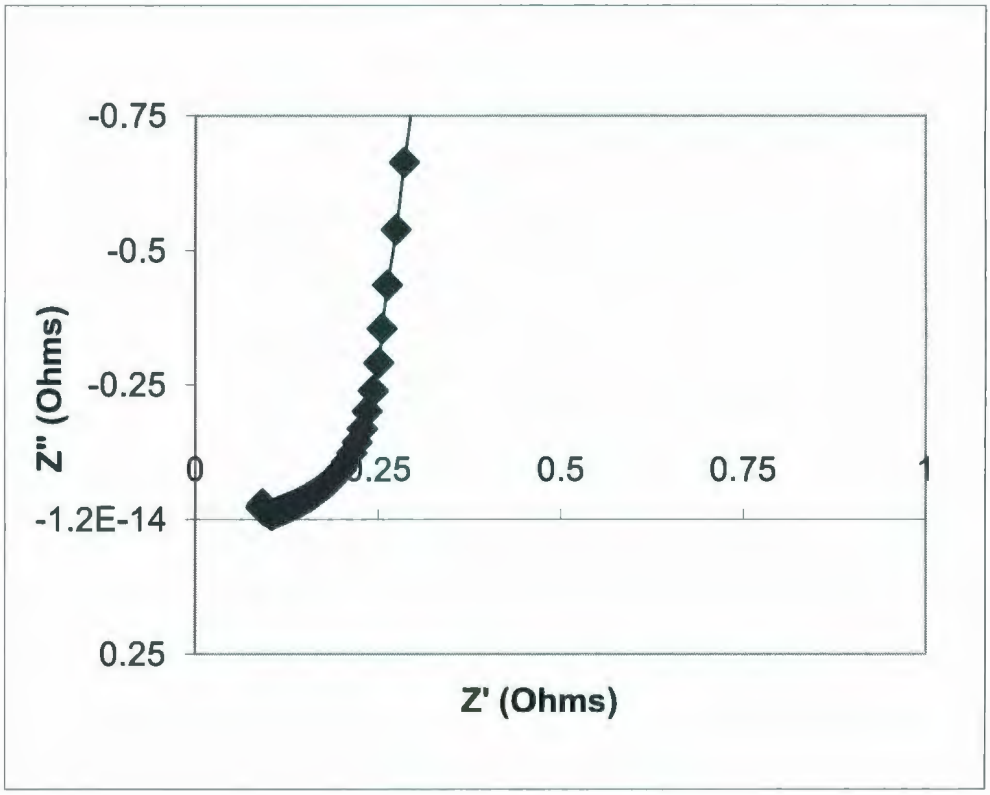


Figure 3.23B: An IS of a SG dough electrode after soaking



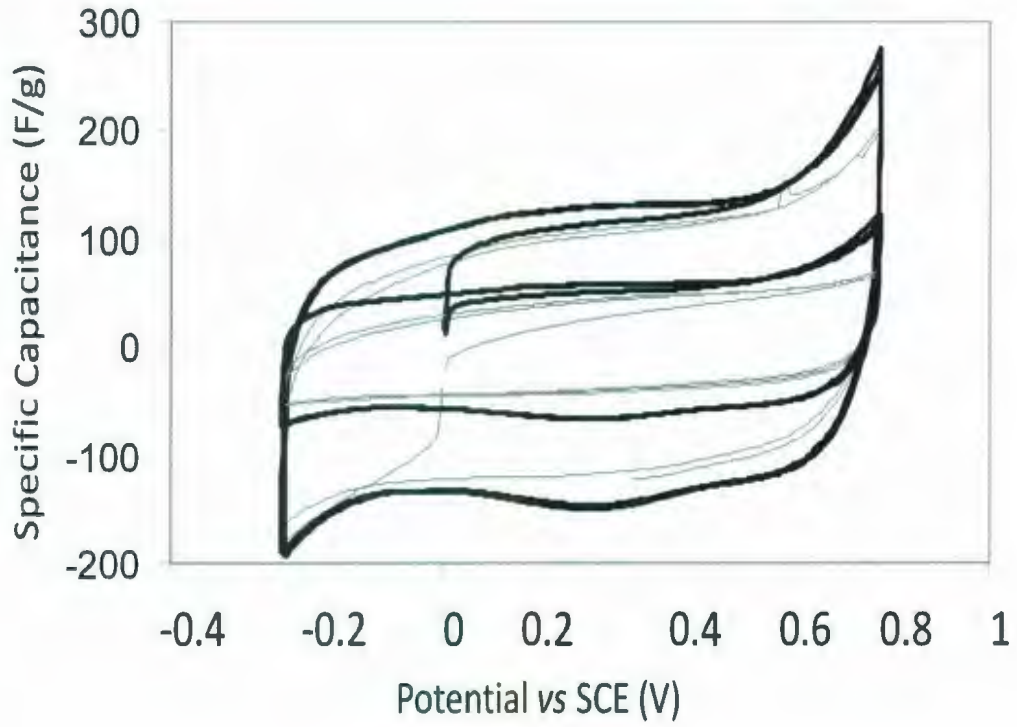
Three more of these types of electrodes were tested by CV before and after soaking in H_2SO_4 giving peak specific capacitances as shown in table 3.8 (the difference in the Cs values of the electrode from figure 3.23 are shown for comparison). The average increase in the Cs after soaking was 21 +/- 10 %. The CV's are shown in figure 3.24.

Table 3.8: Table showing change in Cs after soaking in acid

Electrode	Cs (F/g) before soak	Cs (F/g) after soak	Difference (%)
1	109	124	13
2	44.3	64.6	31
3	113.5	140	19
4.19*	107	321	66

* is probably an anomaly for this test

Figure 3.24: CVs of BP + SG dough electrodes before (—) soaking in acid, and after (—) soaking in acid.

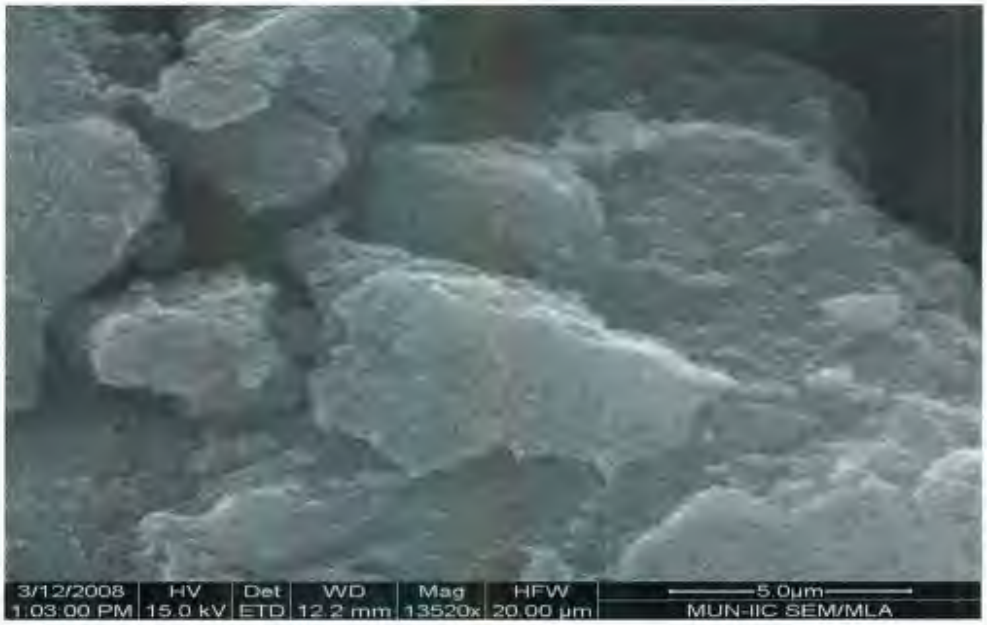


3.4.2 Carbon Dough Structure

Two SEM images of the carbon dough electrodes were taken at increasing magnifications and are shown in figures 3.25A and 3.25B. As with the previous SEM images, the binder (binders in this case) is shown to be combining many minuscule individual particles into substantial particles (aggregates).

Figure 3.25A: SEM image of a carbon dough electrode at 270 times magnification

Figure 3.25B: SEM image of a carbon dough electrode at 13520 times magnification



3.5 OTHER FORMS OF CARBON

A couple of other forms of carbon, Norit SX Ultra (NSU) and Ketjenblack ED600JD (KB) were tested in a small number of experiments with IS and CV. Representative CV and IS results for the NSU are shown in figures 3.26A and 3.26B. As can be seen the NSU electrode displays very similar electrochemical properties to BP, but the average peak Cs value (achieved by running a few more tests) was marginally (~10%) lower than that of the aforementioned BP. The Ketjenblack electrodes were tested exactly the same as the NSU and similar results were obtained.

Figure 3.26A: A CV of a NSU electrode weighing 1.09 mg

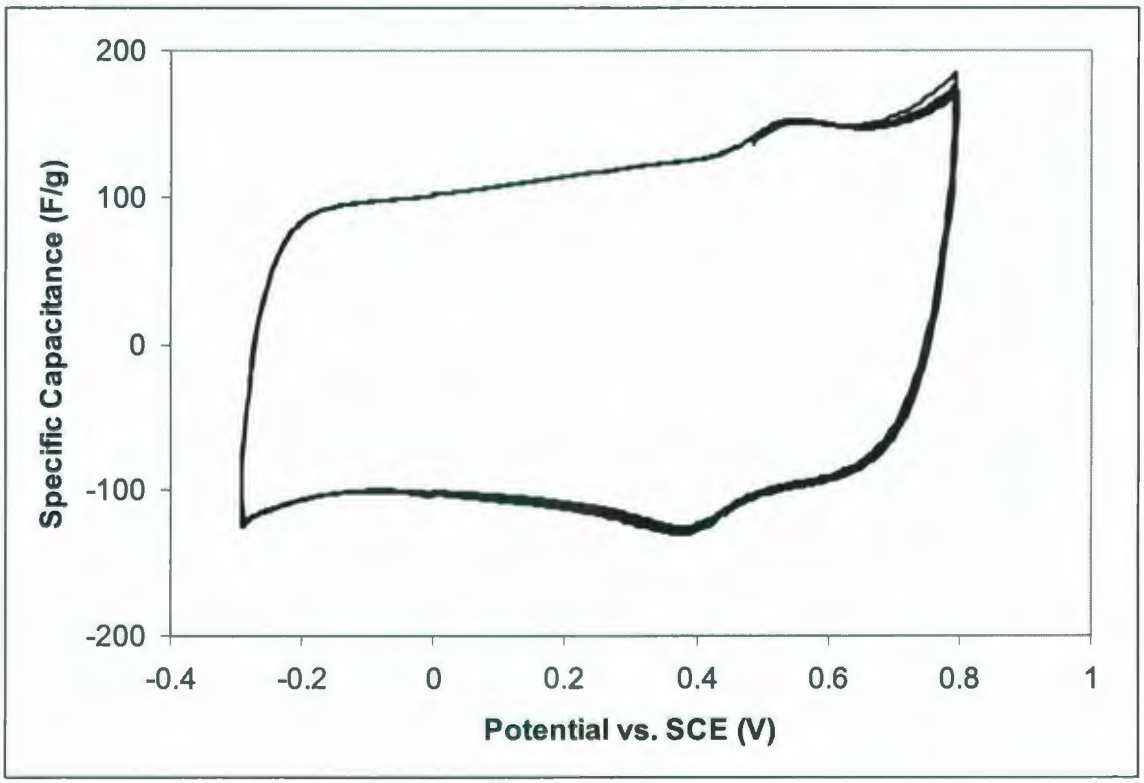
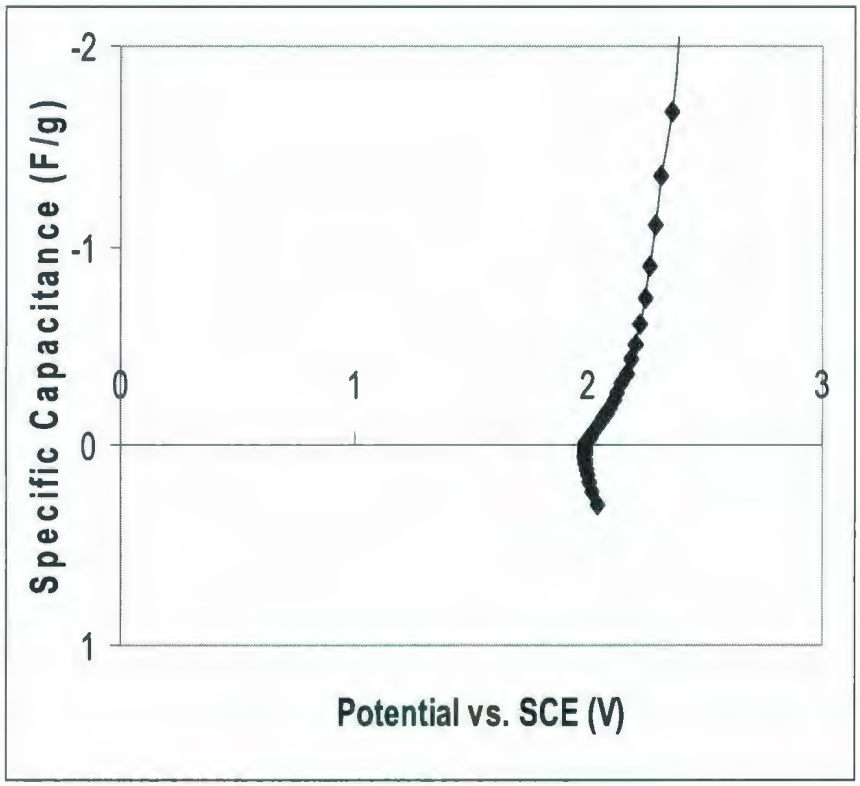


Figure 3.26B: An IS of a NSU electrode weighing 1.09 mg



3.6. CONCLUSIONS

The Nafion percentage added can contribute significantly to the capacitance value obtained, and it was shown that Nafion contributed to the Cs value greatly when compared with SG. And while in this work the optimum Nafion % was found to be 1%, usually 5% is used.[7,9] As can clearly be seen from this chapter the total resistances found when using the conventional and the sandwich cell, with identical electrodes, are vastly different; this is due to the fact that in the sandwich cell the electrolyte resistance is minimized by the very small gap (due only to the Nafion membrane) between the electrodes. Comparing figures 3.4B and 3.9B, the difference can obviously be seen with 3.4B being considerably (>2.2 Ω) more resistive. The new cell design greatly reduced the cell resistance, when compared with the old cell the resistances were usually over 5 times less (going from ~2.0 – 3.0 Ω to 0.3 – 0.5 Ω) leading to much more accurate results.

Another important feature noticed was that the carbon dough method lead to very high mass loading electrodes possessing acceptable Cs (F/g) and R (Ω) values, and while no specific studies were done, the high capacitance values indicate that the supercapacitor would provide excellent energy and power outputs.

While the carbon dough leads to the highest Cs (F/g) the underlying material was still the BP. Even when the dough method was not used BP still achieved an impressive Average specific capacitance of 136 +/- 18.5 F/g was achieved. When the dough method was used with Black Pearls an optimum specific capacitance value of 321 F/g was achieved

References:

1. Frackowiak E., *J. Brazilian Chem. Soc.*, **17,** 6 (2006)
2. Prabaharan S.R.S., Vimala R., Zainal Z., *J. Power Sources*, **161**, 1 (2006)
3. Pandolfo A.G., Hollenkamp A.F., *J. Power Sources,* **157**, 1 (2006)
4. Wu F., Xu B., *New Carbon Mater.*, **21**, 2 (2006)
5: Kolyagin G.A., Kornienko V.L.., *Rus. J. Appl. Chem.,* **80**, 8 (2007)
6. Toupin M., Belanger D, Hill I R, Quinn D, *J. Power Sources.,* **140**, 1 (2005)
7. Liu X.R., Pickup P.G., *J. Power Sources,* **176**, 1 (2008)
8. Valente Nabais J. M., Canário T., Carrott P. J. M and Carrott Ribeiro M. M. L. , *J. Porous Mater*; **14**, 2 (2007)
9. Klotzbach T.L., Watt M., Ansari Y., Shelley D. Minteer D. S, *J. Membr. Sci.,* **311,** 1-2 (2008)

Chapter 4: CARBON FABRIC

4.1 INTRODUCTION

This chapter focuses on the use of a commercial carbon fabric in supercapcitors. Spectrocarb 2225 – Type 925 (CF, Carbon Fabric) is an activated cloth like carbon having a very high surface area (2500 m^2/g specified by the supplier). This material also has good mechanical stability (i.e. the particles are physically stable within the fabric) when compared with the carbon powders.

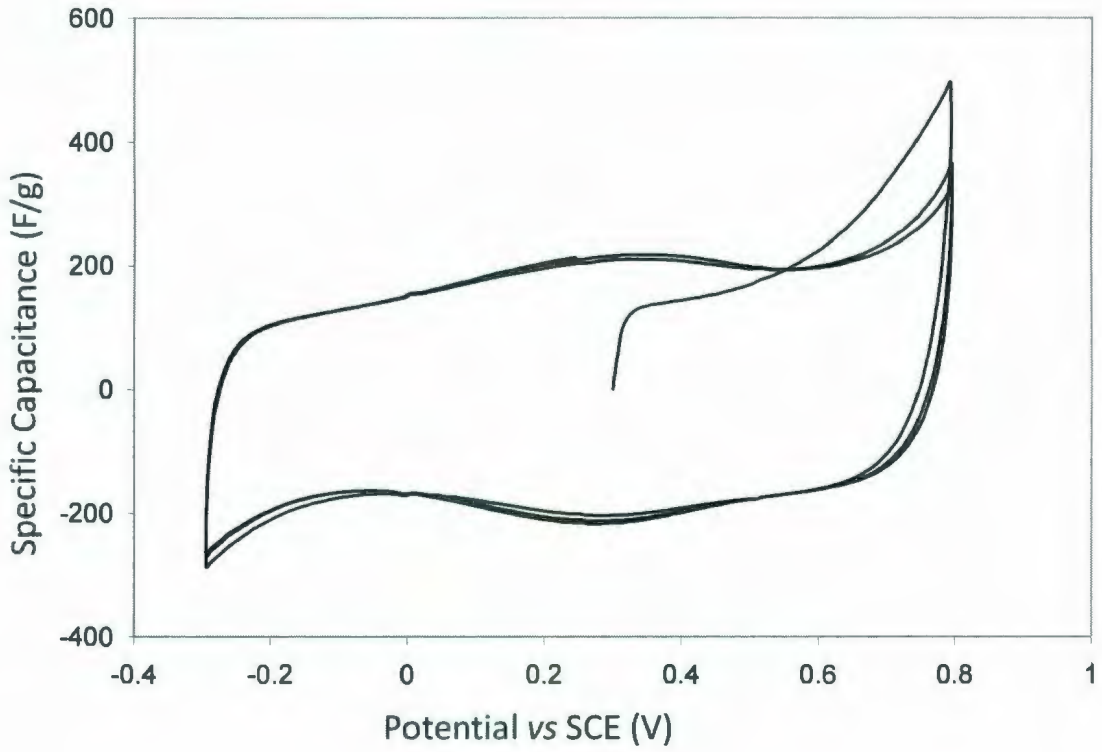
4.1.1 Experimental

The CF was used as an electrode material as follows. A 1 cm^2 circle was punched from a large sheet of CF and placed in a sandwich cell (See figure 2.2b) as the working electrode with a Nafion separator between it and the counter electrode, which was another (slightly larger) piece of CF. This cell was placed in a suitable electrolyte and tested via cyclic voltammetry (CV) and impedance spectroscopy (IS). Details are provided in chapter 2 (2.3).

4.2 INITIAL EXPERIMENTS

In the preliminary experiments a CF disk with no SG was tested and a peak Cs value of 216 F/g was found; figure 4.1 depicts a typical CV. As was explained in chapter 1 the peak Cs is found from a cyclic voltammogram by taking the currents found at the peaks at 0.3 V for the forward a reverse scans dividing by the scan speed and the mass of the electrode. The average current calculated between the two peaks is recorded.

Figure 4.1. A cyclic voltammagram of an unmodified Spectrocarb disk.



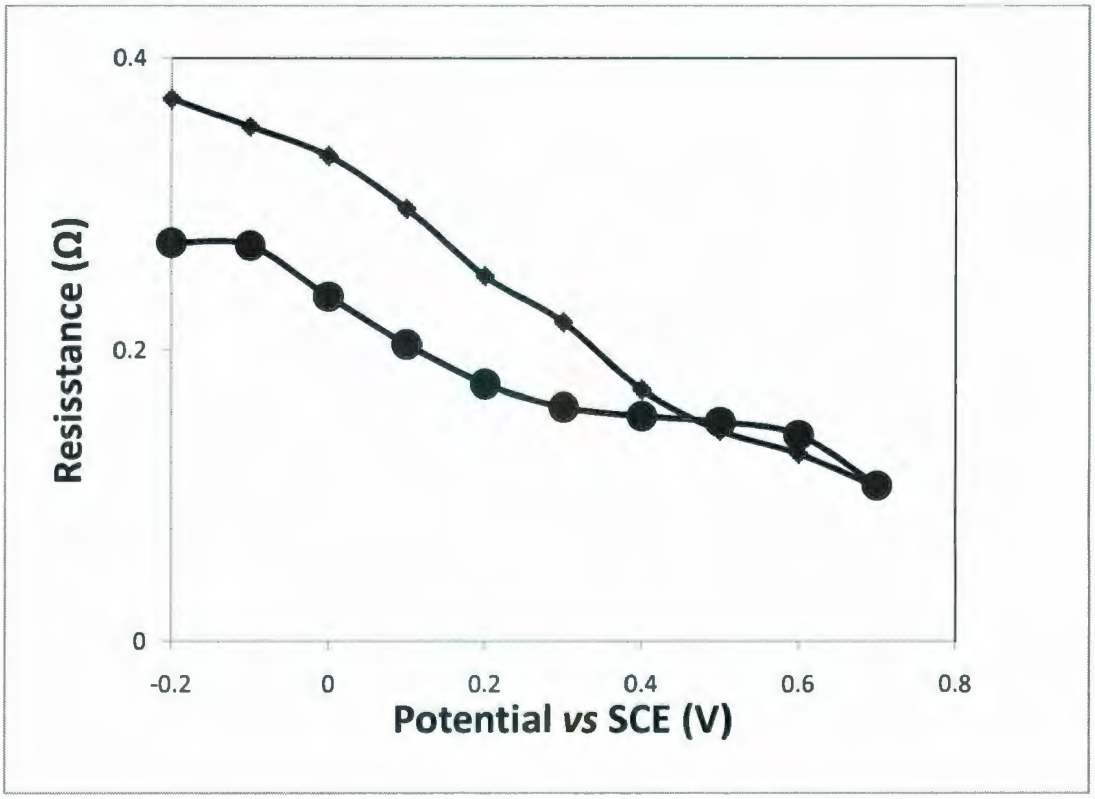
The resistance was somewhat high for the sandwich cell, so the cell was thoroughly cleaned, with the titanium plates that bridged the area between the electrodes and the current collectors, being polished with sandpaper. In addition the cell was put together more tightly. When these techniques were implemented the resistance was lowered substantially, but it was still thought that it could be lowered further. Through impedance measurements (see table 4.1) it could be seen that the majority was due contact resistances. A disk of CFP (carbon fibre paper) was therefore placed between the titanium plate and the CF working electrode, since this was known to give a good contact with the Ti. This solved the resistance problem, and a value of $< 0.3\ \Omega$ was then routinely

obtained. Please note that all other experiments (except those reported in section 4.3) with CF used this method.

4.3 POTENTIAL DEPENDANCE

It was desired to observe how different characteristics of the electrode varied with potential. In an experiment, two CF electrode weighing 14.8 mg, and 15.3 mg were tested using IS, which was performed on each of these electrodes several times with the potential at which the experiment was performed changed each time. Table 4.1 shows results for these 3 electrodes, where potentials are relative to the SCE reference electrode, C is capacitance in Farads and Est R is the total (estimated because an unideal behavior was observed) charge transfer resistance in Ohms.

Figure 4.2: Some resistance values of 2 different CF electrodes tested at different potentials (*vs.* SCE).



This plot shows that there appears to be a relationship between the potential the experiment was performed at and the capacitance obtained. The results came from only two electrodes where the higher potentials were tested later in the day (i.e. the electrode had soaked in the acid longer). However, this data shows that there is not a major dependence on the potential and as CV shows that the Cs should peak around 0.300 Volts; this is due to the formation of *quinone groups* (change in structure) this potential gave the highest peak capacitance, it was used in all future experiments.[1,2]

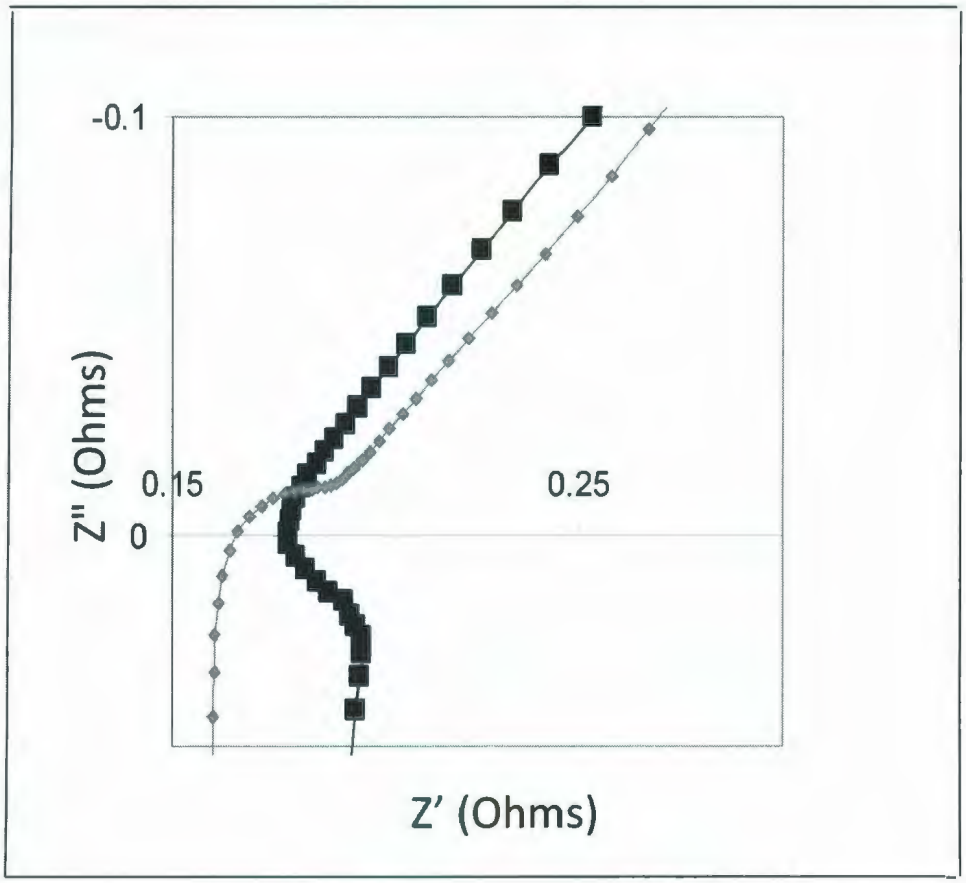
4.4 PLACEMENT OF THE REFERENCE ELECTRODE (RE)

A great number of experiments have proven that the placement of the RE can vastly affect the accuracy of electroanalytical results. This is justified by realizing that an uneven current distribution manifests itself unless the RE is in the exact centre.[3] This section describes the *attempts* at a solution to the problem of the WE (WE1) and the CE (WE2) of a symmetric cell giving different impedance results. Initially, the resistance values that were achieved for two CF disks within a single cell were slightly different as the RE was closer to the CE disk than the WE disk. The first thing that was tried was simply to change the position of the RE between experiments (i.e. make it equidistant from each CF disk). This did not solve the problem, so in the next set of experiments the two CF disks (with SG mashed into them) were soaked in H_2SO_4 prior to the experiment. They were then left to air dry (to allow solvent evaporation) for ~1hr. Then they were tested by IS; a slightly higher capacitance was displayed (as is always the case when carbon electrodes are soaked in the acid prior to the experiment) but significantly

different results were obtained for the two electrodes. These two electrodes should have given very similar spectra as they were contained in the same cell just on different sides. Another two experiments were run using two different cells each containing a larger (1.5 cm^2) CF CE. Again while the results should have been the same they were slightly different.

The cell was then modified by drilling a 1mm hole in each side (see figure 2.2C) in order to allow the electrolyte easier access to the CF. As the results with 1 mm holes were not improved, the holes were enlarged to 3 mm. It was thought that the larger holes would speed up the rate at which the electrolyte could reach the CF electrodes, thus minimizing the influence of the RE, but this did not help the problem much. To better try and equalize the effect the RE was having on the two electrodes, a lugging capillary (a hollow, thin, glass cylinder) ran the electrolyte near the RE to the back and centre of the CF disk used as the working electrode. However, a difference was still observed between the two CF discs, as can be seen in figure 4.3.

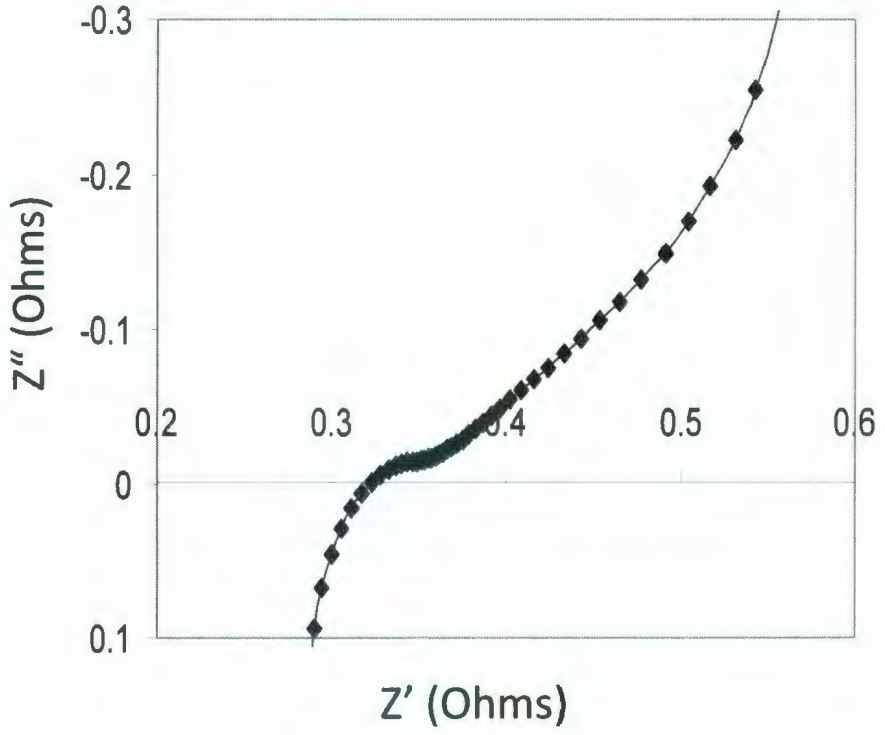
Figure 4.3 IS of two separate yet identical CF electrodes where a lugging capillary was used.



4.5 TWO-ELECTRODE MODE

As a result of these diagnostic tests it was concluded that experiments should be run in "two electrode" mode, without a reference electrode. In this mode the RE lead is connected to the CE.[5] Hence, both electrodes (*a* and *b*) contribute to CV and IS and the capacitance is given by: $\frac{1}{C_{ab}} = \frac{1}{C_a} + \frac{1}{C_b}$. An example of an IS is seen in figure 4.4.

Figure 4.4: IS spectrum, taken in 2-electrode mode, of a cell with two similar CF electrodes

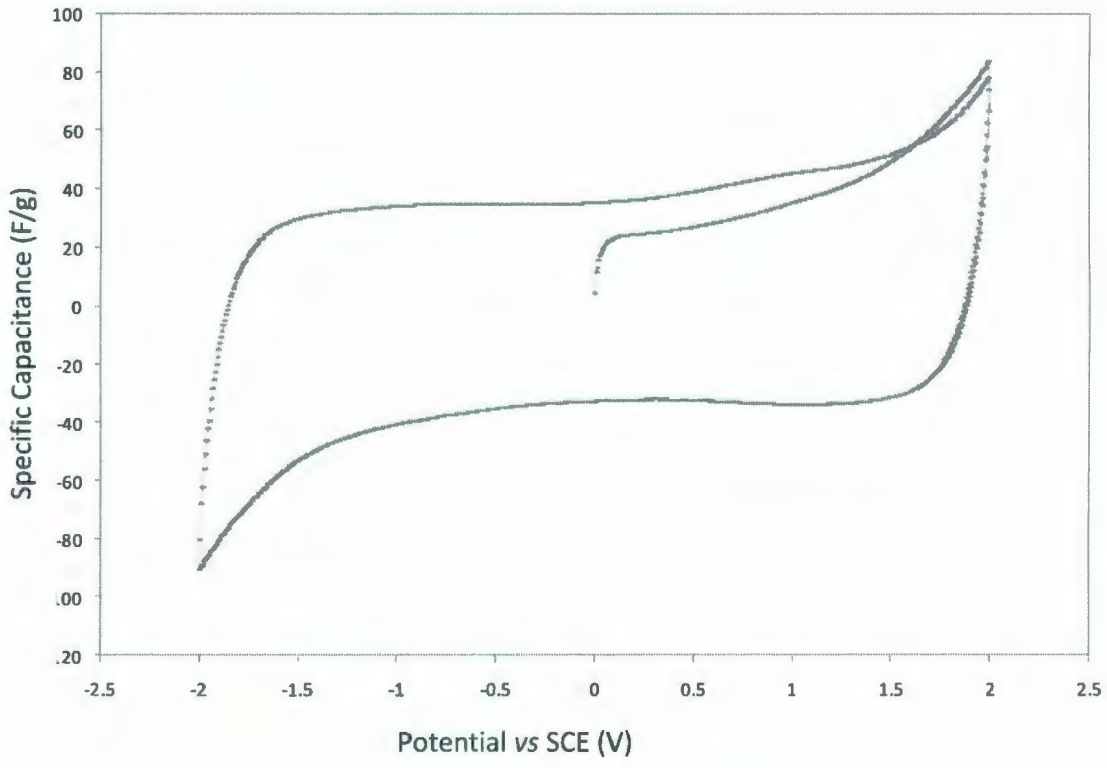


4.6 ACETONITRILE ELECTROLYTE

Non-aqueous electrolytes such as acetonitrile are well known to have been used to test capacitance and can be used throughout a larger potential window as the oxidation from water is eliminated. In the experiments performed in this work, acetonitrile was combined with 1 M $TEABF_4$ to provide the ions needed for conductivity. This was first

tested in the plexiglass cell used for the acid electrolyte. The results (i.e. Cs and impedance) seemed normal but the acetonitrile severely degraded the cell. In order to remedy this, a new cell (figure 2.4D) was constructed that used the same basic design, but with a more chemically resistant PFTE body. Figure 4.5 shows a CV of a CF electrode massing 13.6 mg tested with the non-aqueous electrolyte. As can be seen by the following figure, the potential range over which this electrode could be tested was relatively large; this is due to the fact that acetonitrile cannot be oxidized or reduced easily. This extended potential range may have great industrial applications, as the range can be a major limitation.[6]

Figure 4.5 CV of a CF electrode tested with the non aqueous electrolyte.



4.7 ACID EXPOSURE DEPENDANCE

As was mentioned in the previous chapter, when a carbon powder based electrode is soaked in H_2SO_4 prior to the experiments the capacitance increases greatly. CF also benefits from pre-experiment electrolyte soaking. Figure 4.6 displays the IS of a CF electrode before it was allowed to soak in the acid electrolyte while figure 4.7 shows this results after soaking. While the resistance was low before (~1.2 Ω) from figure 4.6, figure 4.7 shows a substantial drop in the resistance of the same electrode after soaking in H_2SO_4 for 1 hour. A value of about 0.75 Ω was later obtained; this may be very useful for commercial applications.[7]

Figure 4.6: The IS of a CF electrode before acid soaking

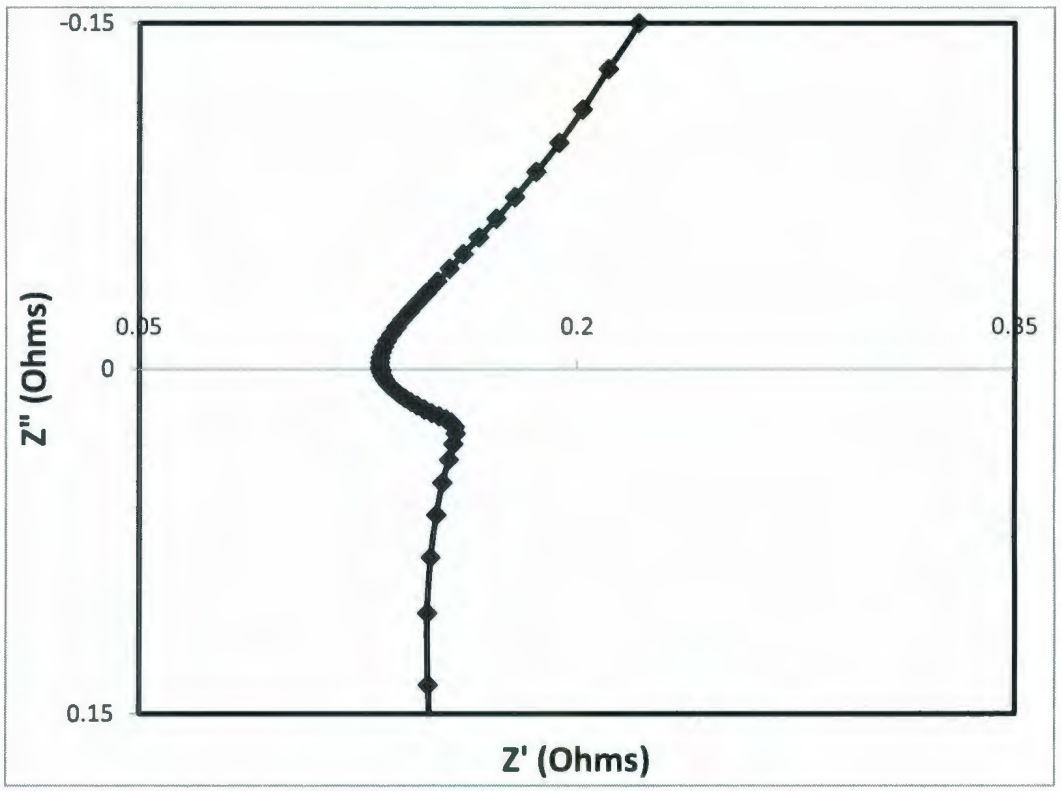
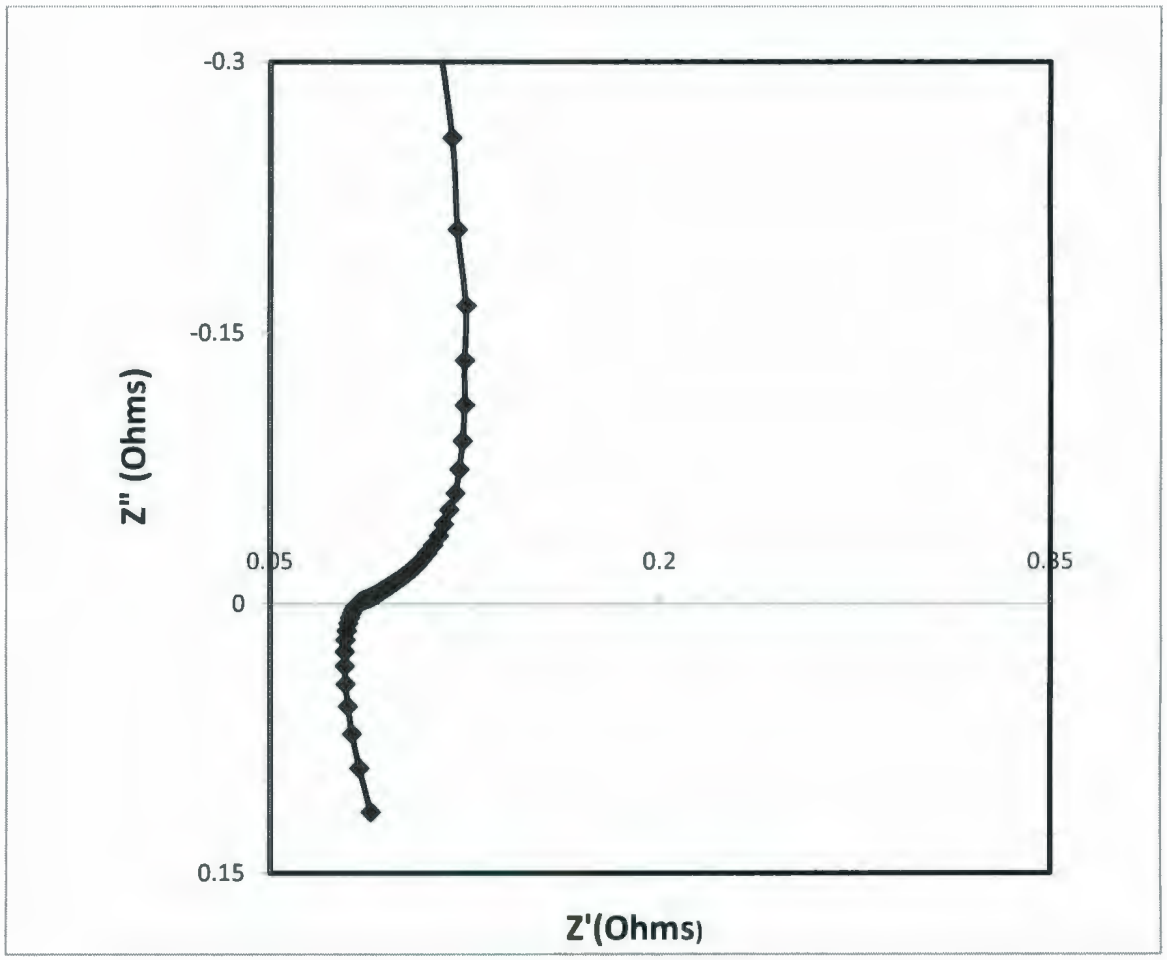
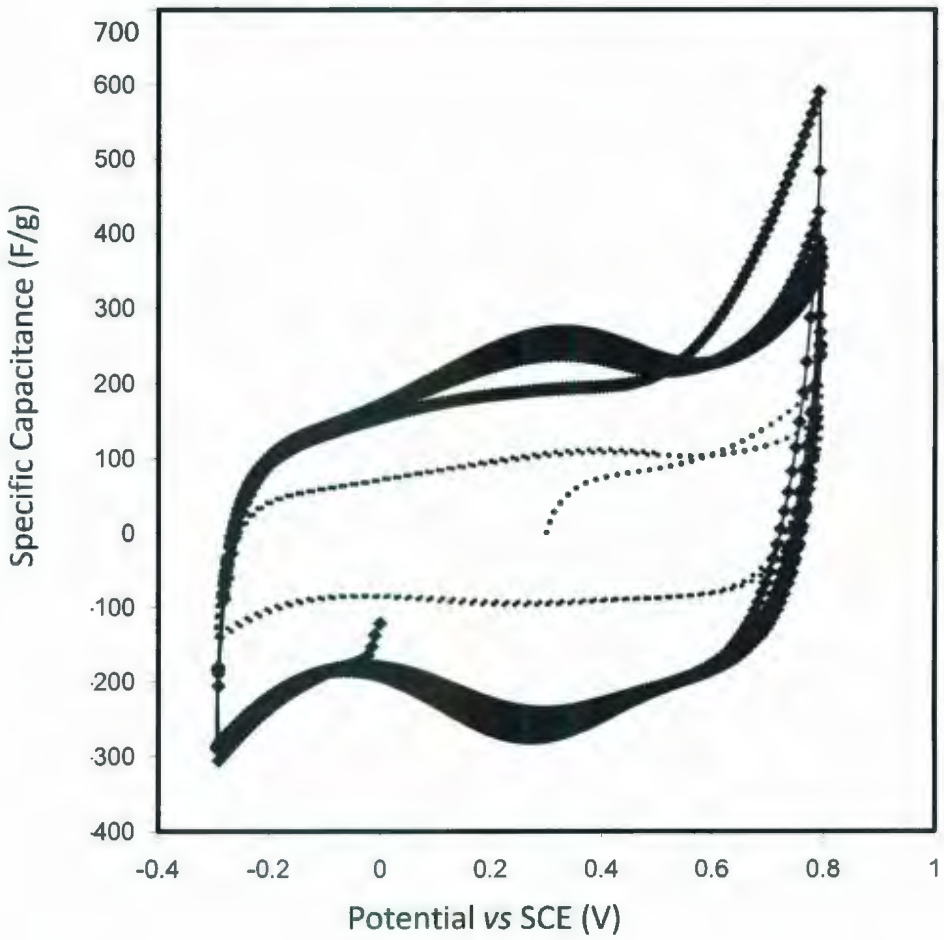


Figure 4.7 The IS of a CF electrode after acid soaking for 1 hr.



Besides the lowering of the resistance, it was shown in chapter 3 that soaking in the acid electrolyte can also greatly increase the capacitance of carbon powders. Figure 4.8 shows CV results for two CF electrodes, one soaked and one not. As can be seen, soaking in the acid greatly increases the Cs of the CF electrodes from 98.0 F/g to 258.5 F/g. This huge leap is due to the aforementioned formation of quinine groups.

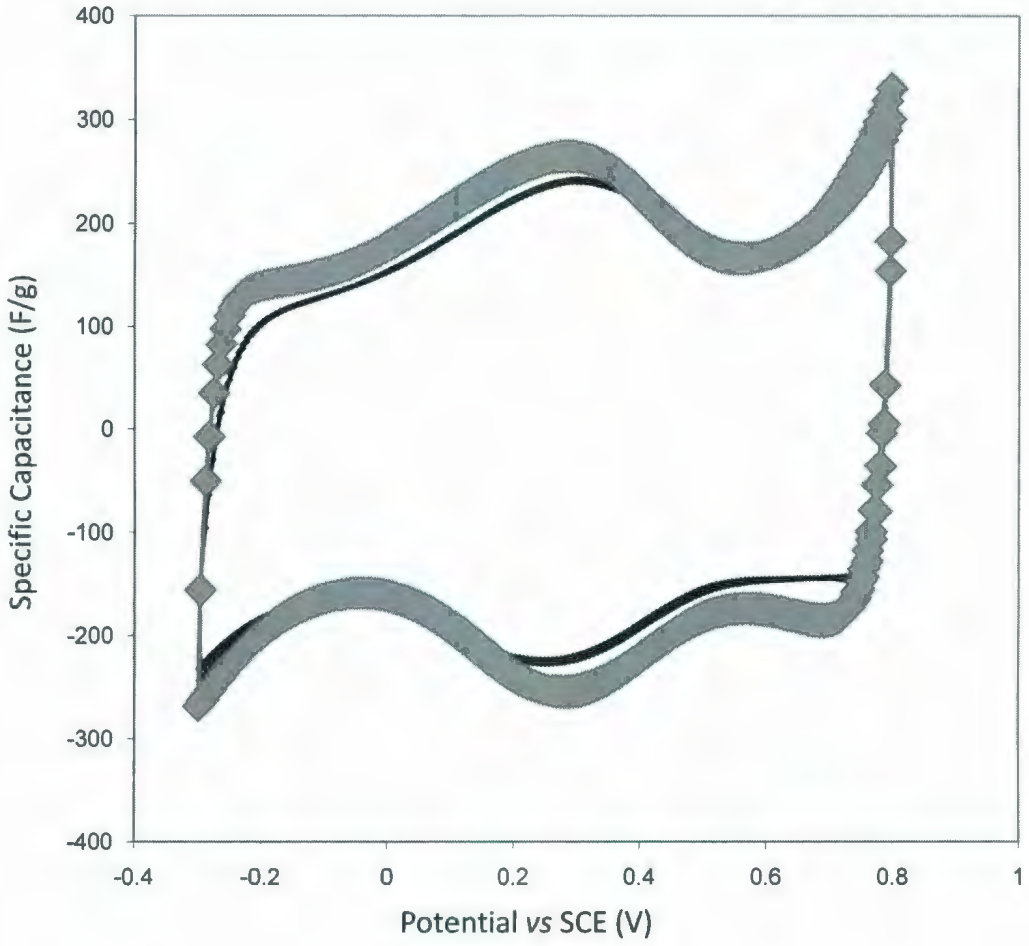
Figure 4.8: The Cs of an acid soaked (solid line) and a non-soaked (dotted line) CF electrode



4.8 ORMASIL APPLICATIONS

SG was used as an additive for some of the CF electrodes by placing them in the ormasil solution while it was still a liquid. These electrodes were then taken out of the ormasil solution and allowed to dry, thus making the SG within the electrodes. These two electrodes massed 29.4 and 39.7 mg, respectively, showing that a significant percentage of SG was present in each electrode (note that all CF electrodes were the same size, with unmodified masses between 13.6 and 14.3 mg). CVs of these electrodes are shown in Fig. 4.9. Their Cs's (based on just the mass of carbon) were 229.2 F/g for the 29.4 mg electrode and 260.1 F/g for the 39.7 mg electrode. These results indicate that the SG has a similar effect on the Cs as soaking in acid.

Figure 4.9: CVs of two CF electrodes infused with SG, the thick ▮ represents the one massing 39.7 mg while the thin – represents the electrode massing 29.4 mg.



4.9 CONCLUSIONS

Experimental procedures were optimized to allow the study of carbon fabric in sandwich cells. When initially tested, a high contact resistance was observed. To remedy this problem a small (1 cm^2) disc of CFP was inserted between the CF and titanium leads (see figure 2.2 B). This almost eliminated the contact resistance. It was determined the resistance could not be measured accurately with the use of a reference electrode in a cell containing two CF electrodes. The capacitance of the CF was enhanced by the techniques of soaking the disks in H_2O_4 prior to the experiments. Another way the capacitance was increased was by the use of the SG, as a proton conducting additive this was quite effective. A much wider potential range was achieved when the CF was tested in acetonitrile, however the highest Cs was determined to take place at 0.300 V in the 1.0 M H_2O_4.

References:

1. Bruice P.Y.; **ORGANIC CHEMISTRY: 2nd Edition.** Pearson Prentice Hall; Upper Saddle River, New Jersey (1998)

2. Berg J.M., Tymoczko J.L., Stryer L.; **BIOCHEMISTRY: 5th Edition.** W. H. Freeman and Company; New York (2002)

3. Adler, SB; Henderson, BT; Wilson, MA, et al. *Solid State Ionics,* **134,** 1 (2000)

4. Raistrick I. D. *Electrochim. Acta,* **35,** 10 (1990)

5. Chen L.C., Ho K.C. *Electrochim. Acta,* **46,** 13-14 (2001)

6. Wang J.; **ANALYTICAL ELECTROCHEMISTRY**. Whiley-VCH: A John Whiley & Sons, Inc.; Hoboken, New Jersey (2006)

7. http://www.answers.com/topic/electrical-resistance-1

Chapter 5: OVERALL CONCLUSIONS

It was seen in this work that very significant capacitances can be achieved with the carbon powders and with Spectrocarb. It was made clear that of the carbon powders Black Pearls was the most useful, and when the appropriate binder was used a somewhat large capacitance can be achieved. It can also be noted that with the design of the new sandwich style cell the BP (and CF) only caused a very miniscule resistance. This research also showed that the carbon fabric is very useful (as a high mass loading is much more easily obtained than with BP), but does not generate a greater Cs than BP at its finest. With BP the largest Cs value that was achieved was 321F/g while Spectrocarb was only able to achieve 258.5 F/g, however the Spectrocarb is much easier to use. So while the BP is better from a purely academic point of view, both may turn out to be very useful as materials for use in supercapacitors It was also shown that Nafion was a useful binder for supercapacitor electrodes and that a proton conducting sol-gel could also improve the properties of supercapacitor electrodes. Another of the major accomplishments of this work was the development of new cell that reduced the cell resistance dramatically. As mentioned in chapter three's conclusion a 2.2 drop in resistance (Ohms) was observed with the employment of the new sandwich cell (figure 2.2b). As demonstrated earlier the technique of soaking an electrode (BP or CF) can greatly increase the capacitance, one theory being that the acid displaces air within the electrodes, and thus increases the active surface area responsible for the capacitance.

This research can be extended in the future by using different materials, mainly different forms of carbon. In particular Carbon Nanotubes provide unique opportunities due to their structure. The unexpected results of using Teflon as a binder show even

counter-intuitive materials should be tested. Carbon has been shown to be a very practical chemical for use in electrodes and can conceivably be improved in the future.